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NEW ASPECTS OF AN OLD AGRICULTURAL QUESTION.

THE FIXATION OF FREE NITROGEN BY PLANTS.

PROBABLY no question in the history of agriculture has stirred the mind of man more than that which asks: "Whence do plants obtain their nitrogen?" And of late years, when science had apparently succeeded in giving a very definite and complete answer to the question as regards most plants, and in showing that the question itself raises a number of others which must be attacked separately before we can hope for the answer as regards others, a gradually culminating storm directed on what appeared to be the last stronghold to be conquered has been slowly organised from various directions, and brought about a conflagration of hypotheses and suggestions which promises not only to break down or blow up the citadel in question, but to light up the territory around so brilliantly, and from so many sides, that its aspect will be entirely changed. From the ruins of the old ideas the new agriculture will arise.

We are told (2) that the Romans were aware of the fact that impoverished agricultural land could be enriched by growing beans, lucerne, and other papilionaceous plants on it for a season, and that the addition of manure was not necessary; and it is evident that a belief in the efficacy of certain crops as soil improvers has prevailed at various times in different countries.

It is clear, however, that no definite ideas of import-

ance to us now could exist before the discoveries, towards the end of the last century, which led to the foundation of that central scientific doctrine around which the whole practice of agriculture must revolve, *viz.*, that the green plant is a living focussing engine, which concentrates energy, in the form of solar radiations, and packs it away in its combustible substance in a latent or potential form, capable of being made to do work at a later time, and in another place.

Only after a series of brilliant chemical pioneers had discovered the existence and properties of oxygen, carbon, hydrogen, and nitrogen, and the composition of water, carbon dioxide, and ammonia, while equally important physiological discoveries had explained the primary functions of green leaves and their relations to light and air, was it possible to begin building up—laboriously and with many slips at first—our present theory of nutrition (3).

This theory can hardly be said to have obtained firmness until Sach's splendid demonstration, about thirty-five years ago (4), proved that the fulcrum on which all turns is the construction of carbo-hydrates in the chlorophyll apparatus of the green plant.

Chemical and physiological theory were then in a position to see more clearly than ever before that, given, on the one hand, a practically limitless supply of carbon-dioxide and water in the environment, and of available energy in the form of solar radiations, and, on the other hand, a living machine like the green plant capable of so directing this energy on the carbon-dioxide and water brought together in its cells that the greater part of it is stored for the time being in the molecules of carbo-hydrates, resulting from the decomposition of the carbon-dioxide and water, you have a real source of wealth which can be theoretically calculated in scientific units, and expressed in the only terms which really mean access of wealth.

Every grain of starch or sugar or other carbo-hydrate thus formed is capable of liberating a perfectly definite and measurable amount of energy, the amount locked up in it from the sun; and it does not matter whether this energy

was locked up ages ago in the coal now brought to our doors, or a century ago in the wood we are now burning, or some months ago in the potatoes or bread we eat to-day, or only a day or hour or two ago in the grass our sheep are feeding on, the fact remains that just the energy locked up in the material in question at the time it was formed is the maximum amount obtainable, and it constitutes the real gain of wealth obtained from the outside universe, condensed on to our sphere of action by the green plant.

But another point began to be clear as the establishment of the above truth became firmer, namely, that these carbon-compounds are the starting products for the synthesis of the much more complex nitrogenous compounds of which living structure is formed. Somewhere and somehow in the living cell, the carbon-compounds referred to are brought into contact with nitrogen, and traces of other elements (of which sulphur and phosphorus are the most important), and worked up into the higher nitrogenous bodies so remarkable for the extraordinary quantities of energy they are capable of liberating, and, what is more important, of economically utilising.

Physiologists have shown clearly that in order to obtain the energy necessary to work this apparent miracle of synthesising nitrogenous compounds from carbo-hydrates and nitrogen, the living machinery of the cell oxidises and burns back into carbon-dioxide and water, part of the excess of the stored carbo-hydrates themselves—the cell thus respire, and in this respect behaves as does any living cell of an ordinary animal.

Having shown that the functions of the chlorophyll apparatus—to manufacture carbo-hydrates from carbon-dioxide and water, by means of the energy of solar radiations, oxygen escaping free—are not only not contradictory of those of the oxygen-respiring living cell—where the burning of part of the gained carbo-hydrates to carbon-dioxide and water occurs as in an animal cell—the path was now clear to inquire into the question of the nitrogen employed in the further syntheses of the more complex substance built up at the expense of the carbo-hydrates.

What could be more natural in seeking for the explanation of the supply of nitrogen, than to turn to the ocean of free nitrogen in the atmosphere as the source of this element?

Recourse to rigidly controlled experiments in the hands of Boussingault (5) and of Lawes and Gilbert put beyond all doubt, however, that *under the conditions devised for these experiments in closed apparatus*, the typical agricultural plants such as beans, peas, wheat, barley, potatoes, etc., assuredly do not "fix" or directly make use of the free nitrogen of the atmosphere, but must have their nitrogen presented in some combined form, and especially as nitrates; whereas they do manufacture carbon compounds out of the carbon-dioxide and water.

It is extremely instructive and interesting to examine the controversies which raged around these questions, and to see how sound was the basis of pure experiment on which their settlement was made.

The only possible conclusion as regards the nitrogen supply seemed to be that it depends on three principal sources: (1) Mineral results of decomposition of rocks, ejecta from volcanoes, subterranean springs, etc.; (2) the products of decay of animal and vegetable bodies, and (3) the ammonia and nitric acid brought down in rain, and principally furnished by the results of electric discharges in the air.

In fact, the green plant seemed to depend for its nitrogen entirely on nitrates, or compounds convertible into nitrates, absorbed by its roots and carried in the water supply to the seat of activity where the higher nitrogenous compounds are synthesised, and although we now know that this statement is too wide, it serves as the basis of the general argument.

Meanwhile and as time went on, a number of discoveries and generalisations in various directions in botany were having their bearing on the question.

Parasitic and saprophytic plants were, of course, dependent on green plants for their supplies of organic materials, and the former especially were dependent on other organisms for their nitrogenous compounds, just as animals are.

The study of the insectivorous plants, especially by Darwin (7), showed clearly that, in some cases, at any rate, there exists arrangements for acquiring nitrogen very directly from animal bodies.

All these examples of what may be called small circulations of nitrogen do not really affect the question of the great circulation of this element in Nature, and much concern was expressed by those who asked : Whence come the new supplies of nitrogen to replace the enormous loss which is continuously going on as the nitrates drain into the subsoil, beyond the reach of the roots, and into the rivers, and eventually to the sea ? One of the two things must be happening ; either the surface of the land is becoming slowly deprived of the nitrogen supplies alone available to plants, or the vast extents of untouched prairie-land, forests, etc., in various parts of the world, are kept in balance by the continuous supplies of atmospheric nitrogen compounds due to electric discharge sufficing to cover the loss always going on below.

Many people were not satisfied that this supply of sub-aerial nitrogen compounds was sufficient to cover the loss, even allowing that the slow disintegration of rocks below, and the bringing to the surface of the nitrogen containing minerals by capillarity, action of worms, and other agencies, delayed the final but inevitable loss. Besides, old meadows annually cropped, but not manured, were found to give steady crops. But another set of ideas had begun to influence the matter, starting from what was at first an old point of view, and developing into a doctrine which has done more to revolutionise agricultural science than anything since the explanation of assimilation.

The older observers would have had great difficulty in conceiving of the soil in which plants grow as anything more complex than a mixture of sand, clay, lime, and bits of other dead substances, but a modern botanist realises that it is a far more delicate and intricate medium than that.

The neighbourhood of the finest rootlets of a bean, lucerne, wheat plant, oak, or pine, offers to us a field of research, which only stops short of bewildering our ideas

by its complexity when we remember the extraordinary and fruitful results that have been obtained already during the last two or three decades. First came the recognition of the fact that every fertile soil abounds in microscopic organisms, and this to a startling degree. Taking at haphazard some later enumerations as more reliable than the earlier ones, Beumer (8) found 44,000,000 to 45,000,000 of germs of various kinds in 1 c.c. of sandy humus; Maggiora (9) got 11,000,000 in the soil of fields; and Caron (10) gives up to 15,000,000, and so the numbers proceed.

We may expect about 1,000,000 to 10,000,000 of germs then in a small thimbleful of such soil. What are these germs doing? A few are undoubtedly those of injurious parasites; others are merely the fungi and bacteria which live as saprophytes on the decaying vegetable and animal remains, and their study is bound up with the whole question of the manure heap and the fermentations and putrefactions which bring organic substances back again into the forms of carbon-dioxide, water, and ammonia; yet others are now known from the researches of Schloesing and Müntz (11), Warington (12), Frankland (13), and especially Winogradsky (14), which oxidise ammonia to nitrous and nitric acids; while yet others, as appears from works by Breal, Heraeus, Frankland, Gayon and Dupetit, and especially Giltay and Aberson, and Burri and Stutzer (15), undo the work of these "nitrifying" bacteria, and "de-nitrify," as the ill-chosen term has it, the highly oxidised salts of nitrogen, that is de-oxidise nitrites to nitrates and ammonia, and even to free nitrogen.

In addition to these forms occupied in oxidising ammonia and in reducing nitrates, however, the researches of Berthelot (16) and Winogradsky (17) point to the existence of forms which, *provided there are plenty of carbo-hydrates available*, can fix free nitrogen in their living machinery, and by means of energy obtained from the destruction of relatively wasteful quantities of carbon, compel this nitrogen to enter into synthesis. In the case of Winogradsky's work, and the known ability of the observer, it certainly does look as if he had succeeded in isolating a definite

form capable of forcing free nitrogen into the synthesis of organic compounds in some such way as is hinted at, though we are quite unable to explain the machinery which effects this. The probability is that nascent hydrogen combines with the free nitrogen and ammonia is formed.

In our astonishment at any such processes as these, we must not lose sight of the truth that when a living cell respire, and oxidises large quantities of carbo-hydrate in the process, the respiration is not a mere direct oxidation of these combustible substances, but is a complex physiological process where the energy obtained from the destruction of the carbo-hydrate is unlocked in the living protoplasm and applied in ways which it is true we cannot yet trace, but which we are sure are rhythmical and effective in their action beyond our present powers of imitation.

Where a "nitrifying" bacterium oxidises ammonium-carbonate to nitrite and nitrate, energy is available, and can be employed in doing work in the cell, *e.g.*, forcing other parts of the ammonium-carbonate into the synthesis of organic compounds, and if we are astonished at this usage of ammonium-carbonate, what shall we say to the corresponding oxidation of sulphur or sulphuretted hydrogen by the sulphur bacteria, or of compounds of iron by the bacteria of ferruginous waters? Nevertheless Winogradsky's work has rendered it extremely probable that many such cases will yet be discovered to exist.

As Pfeffer (18) has pointed out very clearly, these cases do not render the bacteria in question any more independent of solar energy than the green plant itself; for the oxygen necessary is in the last case derived from the chlorophyll activity of these plants, and the reduction of nitrates to ammonia is sooner or later referable to the action of living green plants.

After all, therefore, the actions of these "nitrifying" and "de-nitrifying" organisms are just as dependent on the process of synthesis of carbo-hydrates by the green plant, as are the actions of ordinary saprophytes and parasites, and herbivorous and therefore carnivorous animals.

While, then, the investigation of the numerous organisms

in the soil is revealing to us possible sources of nitrogen-fixation undreamt of hitherto, another and really quite different set of researches has culminated in the recognition of the fixation of that element standing on a still firmer experimental basis. No doubt many of the ancient observers knew of the nodules, or fleshy lumps, on the roots of leguminous plants. In any case Malpighi knew of them more than 200 years ago, and Linneus described them on *Lathyrus*. Perhaps the first serious investigation of them was by Lachmann in 1856 (19), and all kinds of opinions were expressed as to their significance, but without understanding them. In 1866 Woronin (20) discovered that their tissues were filled with bacterium-like organisms, and between that date and 1887, the prevailing opinion was that some living organism of the nature of a myxomycete, a fungus, or a bacterium, makes the tissues of the roots its home.

In 1887 I (21) showed that a perfectly definite living organism invades the tissues from the soil, and proved conclusively that this is so because I showed it passing down the root-hairs of beans growing in water-cultures,¹ and explained the relations of the minute bacterium-like organisms which fill the cells of the tissues to the filamentous infecting tube which penetrates the root-hair.

This organism lives symbiotically in the tissues of the root-tubercles, and the truth gradually became clear that not only are these nodules, with their living invaders, not injurious to the leguminous plant, but *the latter thrives far better if they are abundant and well developed*, than if they are few or absent.

It would require a long article to do justice to the large amount of detailed work by various observers between 1870 and 1890, on the structural details of these tubercles, but the principal names concerned in addition to those given are Frank, Brunchorst, Tschirch, Beyerinck, Prazmowski, Viullemain and Prillieux (22), and controversy

¹ I mention this especially because there has been a tendency of late to attribute this discovery of the infecting tube passing down the root-hair to later observers.

turned chiefly on the following points : (1) The specific nature of the living organism, called "bacteroids," in the cells ; (2) their exact relation to the leguminous plant, and what becomes of them when the plant dies ; and (3) their behaviour outside the plant, since it was evident from various observations as well as from the infection *via* the root-hairs, that they pass some time in the soil around.

The outcome was, put shortly, the organism having invaded the root, stimulates the cells deep down in the cortical tissues to divide and form a delicate tissue of hypertrophied cells ; as these enlarged cells multiply the organism keeps pace with them, sending branches into each new cell. Eventually myriads of bacterium-like minute bodies, so generally taken to be true bacteria, but with peculiarities of their own which weaken the assumption, are detached from the invading branches, and fill these living cells. The latter are not killed by the infecting bacteroids, but, on the contrary, show signs of intense physiological activity, accompanied by the destruction of copious supplies of carbohydrates, brought to them from the leguminous plant.

After a time, however, the activity ceases, and the myriads of bacteroids are found to be in part disorganised. Then the now vigorous leguminous plant is observed to absorb the disintegrated contents of the interior of the nodules, including the disorganised bacteroids in part, the rest of the nodule, and a certain proportion of bacteroids which have escaped destruction, being left as *débris* in the soil. There can be little doubt that we have three periods to distinguish here. First, the invading organism is acting as a parasite, but though it lives at the expense of the cells which it has enslaved, and forced to greater and greater physiological activity, it does not destroy them. In the second stage we have a period during which the struggle for existence is evidently extremely intense ; at first the invading organism takes everything the cells can give it, but gradually it passes into a more passive condition, and fills the cells with bacteroids, and all proceeds to a state of comparative rest. Now begins the third stage. The more and more vigorous leguminous plant exerts a draught

more and more pronounced on the passive contents of the tubercle (how far such a draught on some of the contents has been going during the second stage, we cannot say), and everything incapable of resisting solution and absorption is taken up, leaving the nodule a nearly empty limp collapsed shell, in which such bacteroids as have managed to pass into a sort of resting stage alone remain alive to be scattered in the soil around as the *débris* of the exhausted nodule rots away.

It is, at least, certain that the disorganised and absorbed contents thus taken up by the now all-triumphant leguminous plant, are extremely rich in nitrogenous materials; the question is, *can this nitrogen represent any more than the combined nitrogen passed into the cells by the leguminous plant itself*, and which at most has undergone transformations, not affecting its quantity, in the bodies of the conflicting organisms? If so, of course the storage of nitrogen in the nodules would be a mere incident not affecting the question before us.

Between the years 1888 and 1890 a series of papers by Hellriegel and Wilfarth (23) turned public attention to these leguminous nodules from another side. During the progress of a long series of experiments, valuable in many ways to agricultural science, on the nutrition of cereals and gramineous crops as compared with that of leguminous plants, the above authors were, first, again struck with the great differences in these two classes of plants, as regards their powers of accumulating nitrogenous substances, as already noticed by others; and were then led to compare the results, as regards gains in nitrogen by the leguminosæ, with the prevalence and size of the nodules on their roots. They came to the conclusion, which they abundantly supported by experimental results, that of the various hypotheses afloat to account for the gain in nitrogen shown by leguminous crops none was satisfactory, but that, in some way or other, the presence of the nodules was concerned in the matter—for leguminous plants devoid of nodules, or ill-furnished with them, either lead but a starved existence or die altogether, as do gramineæ in any case if no source of nitrogen beyond the free nitrogen of the air is at their disposal.

Hitherto there were four sets of conflicting opinions in the air as to the explanation of the allegation that leguminosæ can accumulate nitrogenous substance in soil so poor in nitrogenous compounds that even if all possible sources of combined nitrogen were taken into account, there is an unexplained balance in favour of the plant.

First, some assumed that the richly-foliaged leguminous plant assimilates *free* nitrogen direct from the air by the leaves: "They obtain their carbon from the air—why not their nitrogen?"

Second, others suggested that the abundant foliage enables these plants to gather up more completely than can other plants, the traces of nitrogen *compounds* always existing in the air, and thus to concentrate this obscure supply.

Third, others pointed to the deep and abundant root system so characteristic of many leguminosæ, and said: "These roots can obtain supplies from the subsoil far beyond the reach of the roots of ordinary plants".

And fourth, many people denied that any difference as to power of obtaining nitrogen really existed between leguminosæ and other plants, but assumed that these richly-rooted plants in some way favour processes of nitrogen accumulation in the soil itself—processes quite independent of vegetable, but in some way produced by physical or chemical fixation in the soil.

The researches of Boussingault and of Lawes, Gilbert and Pugh, already referred to, had refuted the first of these suggestions, and, properly interpreted, may still be regarded as a complete reply to the assertions of Ville, their chief opponent. But we must not forget that the conditions of these experiments *excluded the infection of the leguminous plant*, and that the results obtained were got with plants *devoid of nodules on their roots*.

As regards the second hypothesis, Hellriegel and Wilfarth showed clearly (and others have shown the same) that unless there is some compound of nitrogen in the air not detected by the methods of analysis to date, the gains in analysed peas and other leguminosæ, growing in soils free

from nitrogen compounds, were out of all proportion to the supplies of combined nitrogen from all known sources. This result was only obtained, however, with peas, etc., which had *plenty of nodules on their roots*; similar plants devoid of the nodules passed into a condition of starvation similar to that to which gramineæ succumbed under the same conditions.

The answer to the third hypothesis was supplied by experiments in pots, *where no subsoil existed* to store the presumed nitrogen compounds only available to deep-diving leguminous roots. The gramineous roots had as much chance as those of the leguminosæ to explore the medium, but the results were the same—using the same nitrogen-free soil for both crops, the leguminosæ in some way obtained nitrogen elsewhere, *so long as they had plenty of nodules*.

The fourth hypothesis gave trouble. According to it, as we have seen, the leguminous plant does not itself directly accumulate nitrogen from the air, but it, in some way, favours processes by which the soil accumulates it and renders it available to the roots.

Traces of combined nitrogen always occur in the air, and can be absorbed by the soil. The dust of the air contains combined nitrogen, and rain is always bringing down this and traces of ammonia and nitric acid formed by electric discharges. Schönbein and others have stated (though it has been disputed) that ammoniacal compounds are formed during evaporation from moist surfaces or combustion in confined air, and Berthelot stated that even electric discharges of low intensity, such as pass between air and soil, can produce nitric acid by forcing the free nitrogen of the air into combination.

Berthelot had already stated, moreover, that micro-organisms in the soil can “fix” free nitrogen, and build it into their bodies; though that view had by no means obtained the acceptance it has since received, being then but feebly supported by experimental evidence.

The *débris* of organisms in the soil is continually undergoing decompositions with liberation of ammonia, and this ammonia owing to the action of porous bodies and alkalies

—to say nothing of the nitrifying organisms now known to be especially effective—is continually being oxidised to nitric acid and its salts.

Against these possible gains of nitrogen to the soil we have to set a series of sources of loss. Although the upper layers of soil can hold certain salts of nitrogen with great tenacity, it is well established that the drainage water carries off large quantities to the depths of the subsoil, and into the drains, rivers, etc., to the sea, and we know that de-nitrifying organisms cause the freedom of certain quantities of free nitrogen from the decomposition of nitrates and other compounds of that element.

It was impossible to trace in detail this complex circulation of nitrogen in Nature, and Hellriegel and Wilfarth's experiments brought the question to this crux.

If leguminosæ and gramineæ are grown side by side in pots, in nitrogen-free soil (or soil in which the known nitrogen contents are small), the gramineæ die of nitrogen starvation: so do the leguminosæ, unless their roots are infected and develop plenty of nodules containing the symbiotic organism. In the latter case the *closed system of pot, soil, and plant gains in combined nitrogen* to such a large extent that there is no doubt the excess of nitrogen comes ultimately from the free nitrogen of the air.

Of the truth of this conclusion I convinced myself by a series of experiments at Cooper's Hill, and it has been abundantly confirmed by many other observers.

The controversies which raged about this time, and in which Frank, Berthelot, Beyerinck, Breal, Lawes and Gilbert, Koch, Nobbe and Hiltner, and Prazmowsky, were especially prominent (22), led to extremely useful information and ideas which would carry us too far if examined in detail. The new knowledge did not alter the above position, and the results can best be made clear by shortly summarising the results of experiments by Laurent and Schloesing, Koch and Kossowitsch and one or two others.

Laurent and Schloesing (24) repeated the old experiments of Boussingault and Lawes, Gilbert and Pugh, under the new conditions necessitated by the new knowledge.

They grew plants from seed, leguminous and others, in a sterilised glass apparatus, which may be described as a large test-tube fitted with supply and exit pipes, through which a known atmosphere could be circulated by means of a pump.

The whole system was closed, but samples of the atmosphere could be withdrawn and analysed at any time. The apparatus was a beautiful and ingenious contrivance, and provided for the supply of water and carbon-dioxide to the foliage exposed to the light, as well as for a circulation of air known to consist of oxygen and nitrogen in the free state only, all nitrogen compounds being taken out.

The principle of the experiment was this : Not only was the nitrogen in the seed and soil and in the atmosphere in which the plants were growing known at the beginning of the experiment, but it was also known in the crop, soil and atmosphere *at the end of the experiment*. Consequently any "fixation" of nitrogen by the plant appeared as a balance at the conclusion of the experiment. It would take too long to describe the details, but Laurent and Schloesing proved that not only did the nitrogen increase in the *crop* of leguminous plants, but a corresponding amount had *disappeared from the atmosphere surrounding them*. This result was only got provided these plants were infected with the bacteroids, however, and well provided with nodules, as described above. If no nodules appeared—the bacteroid organism not being added to the sterilised soil—the leguminosæ starved, as did all other plants such as cruciferæ, gramineæ, potato, beet, etc., tried.

At first sight this seems conclusive, but in reality it does not settle the real point at issue. It does prove—and more conclusively than the numerous other experiments which have now placed this matter beyond all doubt—that the nitrogen is taken from the air and must be taken as free nitrogen, but it does *not* settle the question whether this free nitrogen is forced into combination *in the soil or in the leguminous plant* itself, and, if the latter, we have still to ask, is the fixation due to the *bacteroids*, or to the symbiotic compound plant (leguminous plant plus its bacteroids) ; and whereabouts in the infected plant does it take place ?

Frank (25) has long distinguished himself as the chief upholder of the hypothesis that the fixation occurs in the leaves and other sub-aerial tissues of the plant itself ; but although the admirably ingenious experiments of Kossowitsch (26) did not settle the question whether the fixation occurs in the subterranean parts, or in the superterranean foliar region, they did render the latter view the more improbable one. And many considerations prevent our accepting Frank's hypothesis that the symbiotic organism so stimulates the entire organisation of the infected plant that its assimilating cells, in the organs exposed to light, force the nitrogen straightway into combination.

The structure of the nodules, as shown by the researches of others as well as by my own analyses, certainly lends support to the otherwise probable view that whether the combination is effected by the bacteroids themselves, or by the cells infected by them, the actual seat of the action is in the nodules. Large quantities of carbo-hydrates are carried to these cells, a complex and very regular system of vascular bundles connects them with the mother-root, the infected cells show all the well-known signs of intense physiological activity, and it is known that the plant eventually drains the nodules of materials, and leaves them exhausted. That carbo-hydrates, water, and nitrogen come abundantly into contact in these cells, there is no doubt, though we have no measure of the quantities of materials passing to and from the nodules.

On the other hand, all attempts to demonstrate that the bacteroids cultivated outside the plant can assimilate free nitrogen have failed, unless we except the very doubtful results of Beyerinck (27). It is true, we must not lay too much stress on these negative results, because the cultivation of an organism so highly adapted as this must be to its symbiotic life may well fail outside the cells of the host.

Here, then, for the present the matter stands. The infected leguminosæ do bring about the fixation of free nitrogen, but other plants do not ; the fixation occurs in the underground parts of the plant, and not by physical or other processes in the soil, and the seat of fixation is the

infected tubercles. But whether it occurs by means of the stimulated protoplasm of the cells of the tubercle, or by means of the protoplasm of the bacteroids here placed in such circumstances that they can, by oxidising and destroying large quantities of the carbo-hydrates abundantly brought to them, force nitrogen into combination on their own account—as Winogradsky's results suggest that other bacteria can do quite apart from any host plant—must for the time being remain an open question. Meanwhile, however, another aspect of this question of the fixation of free nitrogen had forced itself into the foreground.

In Laurent and Schloesing's experiments it was found that although sterilised soil alone was unable to fix nitrogen, sterile sand on which certain mixtures of common soil, algæ and bacteria were sown did fix it. Frank (28) had previously stated that algæ could fix nitrogen in daylight but not in the dark; and Laurent and Schloesing showed that it was essential that their algæ should not be covered up from access of light, *e.g.*, by a layer of sand.

In all these cases it turns out that we have to do not with the fixation of nitrogen by algæ, but with the action of *symbiotic combinations of algæ and bacteria*, for Kosso-witsch (29) has recently shown that the algæ alone, isolated in pure cultures by Beyerinck's method, are incapable of fixing the nitrogen, whereas if soil-bacteria of various kinds are allowed access to the algæ, in the slimy cellulose walls of which they grow and establish symbiotic unions, considerable, and in some cases very large, amounts of free nitrogen are fixed, and this power is increased by adding to the symbionts *just such carbo-hydrates, viz.*, sugars, as the algæ will provide. These experiments not only throw much light on the whole question, but they possibly enable us to understand Berthelot's results, in which nitrogen-fixing bacteria could only do the work if supplied with plenty of carbo-hydrates, and bring the whole matter into relationship with Winogradsky's results. In fact, as the authors referred to indicate, and as Duclaux (30) has recently pointed out, it looks as if the whole question of nitrogen fixation, whether by bacteria of soil, the nodule

organisms of the leguminosæ, or the symbiotic unions of algæ and bacteria, resolves itself into one, *viz.* : the question of living cells under certain conditions where they can destroy large quantities of carbon compounds, being able to obtain the energy necessary to enable them to force free nitrogen to combine with some of the products.

If this is so, it seems to me there is a question definitely stated for chemistry to attack. The known inertness of the nitrogen molecule seems to have had much to do with discouraging chemical investigation along these lines, and I am told that practically no grounds exist for a deductive explanation of any such process as this seems to imply. Of course we must not forget that objections to hypothetical explanations of physiological experiments have usually been urged at similar periods to that which the nitrogen question is in, and have done good service ; but occasionally, as with Liebig's scepticisms concerning the respiration of plants as a physiological process, persistence in the demonstration that a given result, inexplicable from the chemical point of view, really does take place in the living cell, leads to valuable advances in knowledge.

Evidence has been given to show (33) that we cannot explain the matter by reference to the newly-discovered constituent of the atmosphere, Argon ; and it seems certain that the problem is, at present, insoluble.

At the same time, we must not forget that there are plenty of other cases where the living protoplasmic machinery of a cell carries out analytic and synthetic changes, with economy, which are either inimitable in the laboratory, or only possible at high temperatures, or under conditions which make it mysterious how the cell manages to do the work with, apparently, so small an expenditure of energy—I say apparently, because of course the energy necessary to do the work is the same in both cases, only in the laboratory much has to be wasted owing to the methods of application.

These facts point to a question of the mode of presentment, so to speak, of the molecules concerned, and, no doubt, the chemist will soon learn some method of so bring-

ing the nitrogen molecule into the sphere of action of some carbon compound that the riven molecules of the gas will enter into combination with the latter before they have a chance of again combining among themselves into the ordinary inert form. At the same time the objection suggests itself that if it is all a matter of an active cell over-supplied with carbo-hydrates, why cannot *any* vegetable cell do the trick? It seems probable that further research with anærobic organisms and fermentation may help us to answer this question.

On the other hand, we ought to be very careful before accepting rough agricultural experiments as too conclusive in these matters. This is not in deprecation of the empirical trials so valuable in all pioneer work, and I would emphasise the fact that we are in need of very much more experimental work of the nature of Caron's (10), especially summarised as cautiously as he has done it.

Schultz-Lupitz's (32) experiments have clearly proved that the growth of lupins on poor sandy soils does improve them, and in the course of years brings up the nitrogen contents of these soils to a very valuable amount, and Caron, struck with the general consensus of results indicating that bacteria in the soil have great effects on processes concerned in vegetation, set himself the task of examining the soils to see how far the artificial infection of soil by various bacteria improves the crops and affects the quantity of nitrogen.

Shortly summarised, Caron shows pretty clearly that oats, rye, wheat, etc., yield better results when there are plenty of soil bacteria at work among their root-hairs than when the latter are in a soil not thus infected. Caron himself believes that the bacteria he used fixed free nitrogen, though he admits that the beneficial effects may be due to the bacteria rendering compounds available which would otherwise have remained less so.

I think his experiments give less support than he believes to the first hypothesis, and that he does not clearly show all the possibilities, but there can be no doubt that his results open up a splendid field of inquiry, which ought to be followed up as vigorously as possible, by means of exactly con-

trolled experiments with apparatus such as that used by Laurent and Schloesing, and with the bacteria employed not only cultivated pure (Caron did that), but examined rigidly by the best bacteriological methods.

In any case, as even this brief summary of recent results will show, the problem of the relation of the agricultural plant to soil and air is taking new turns, and it remains to be seen how far the new departures will carry us. If symbiosis, whether intimate, as in the case of leguminous plant and bacteroid, etc., of algæ and bacteria, or remote (for the carbo-hydrates necessary are merely not handed over directly—a point which only makes the symbiosis disjunctive), as in the case of Winogradsky's and Berthelot's bacteria, is so powerful an advantage in the struggle for existence, we may well expect that further research will yield much.

After all symbiotic algæ and bacteria are merely lichens—bactero-lichens if you will; if it turns out that some of the lichens on the bare crags and peaks of primitive rocks behave towards free nitrogen as those examined by Kossowitsch did, we may hope to approach the solution of even deeper problems concerning the circulation of nitrogen in Nature.

Many other problems are before us to which the above results and speculations give new interests. What are the nostoc filaments doing in the cavities they regularly occupy in gunnera, and in the remarkable apogeotropic roots of cycads, where they seem to have made themselves as much a part of the tissues as in a lichen? What effects do they produce on the physiological activity of the colourless cells between which they intercalate themselves? Are these cycad-nostocs accompanied by bacteria, as Reinke and Schneider observed in some cases; and, if so, have we the same thing here going on in the tissues of higher plants as in the algæ and bacteria of Kossowitsch? Numerous other questions of the same kind arise concerning nostocs and other algæ habitually embedded in liverworts and vascular cryptogams, and among the various aquatic plants there are many more examples of mysterious sym-

biotic relations between host and guest, which we may now say await further investigation from the new points of view.

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H. MARSHALL WARD.

THE RATIO OF THE SPECIFIC HEATS OF GASES.

THE Kinetic Theory of Gases is making little progress at present, for want of information regarding the nature and relations of the parts of a molecule. The laws of Boyle, Charles and Avogadro have been fairly completely explained without this knowledge, as have also the main facts concerning diffusion and viscosity, but wherever temperature changes come in there begin to be difficulties. The way in which the viscosity coefficient of a gas varies with the temperature has not been explained, because we do not know the law of force between two molecules, and work on the specific heat is rendered nugatory from our ignorance of the nature of the atoms and their relations to each other.

Consider what happens when a gas is heated. The heat that is communicated to it may take any or all of the following forms :—

- A. Kinetic energy of translation of the molecules as wholes.
- B. Potential energy due to separation of the molecules.
- C. Kinetic energy of the motion of the atoms relatively to the centre of mass of the molecule.
- D. Energy of rotation or vibration of the separate atoms regarded as elastic bodies.
- E. Potential energy due to the separation of the atoms in the molecule.

Perhaps a sixth class should be added containing other forms of energy (electrical, etc.), arising from the relations between the molecules and the ether. About this class little or nothing is known, and whether any serious modification in what is said below would result from taking account of it must remain for the future to decide.

We know that A always takes a share of the heat communicated to the gas. Different molecules will in general have different velocities, and consequently different

amounts of energy of translation, but the mean value taken over a large number of molecules is what is usually taken to represent the temperature of the gas, so that to say that the temperature of the gas rises is equivalent to saying that the kinetic energy of translation of its molecules increases.

The energy in class B is small compared with that in A, but is generally quite appreciable. The most usual conception of a gas is that of a large number of molecules attracting each other with forces that fall off very rapidly as the distance between the molecules increases, so that any one molecule is moving freely in an approximately straight line during the greater part of the time. It is necessary to assume some slight attractions between the molecules, even when they are not very close together, to account for the divergence from Boyle's law, hence on expansion work will be done against these forces, and potential energy will be gained. The amount of this energy is, however, easily calculated, if we know the characteristic equation of the gas, and so it gives us no theoretical difficulty.

The remaining three classes constituting the internal energy of the molecule are the real difficulty. D will be discussed later, and is perhaps so small as to be negligible, or at least constant in amount during changes of temperature. Classes C and E are completely outside any dynamical theory of matter at present. We cannot calculate their amount theoretically until our knowledge of the dynamics of a molecule is very greatly extended, but fortunately we have the means of proceeding in the reverse direction. We can find what proportion of the total energy given to the gas takes the form of C, D and E together, if we know the ratio of the specific heats. The formula by which this is effected is well known to physicists, but it will be well to give the proof in order to show more clearly what it is we really learn from it.

Let C_v be the specific heat of the gas at constant volume, then the heat required to raise the temperature of one gramme of the gas by a small amount δt is $C_v \delta t$. Let δT be the increase in the kinetic energy of translation

of the whole of the molecules, and let $\beta \delta T$ be the energy that is taken up in vibrations of the atoms relatively to the centre of mass of the molecule, and the other forms included in C, D and E. It is not assumed here that β is constant. It is probably not constant in the case of some gases, but at any one temperature and pressure the heat that goes to increase the intramolecular energy will bear some definite proportion to that which increases the translational energy.

We have then $C_v \delta t = \delta T + \beta \delta T$.

Now if we consider what becomes of the heat that is given to the gas at constant pressure, we get—

$$C_p \delta t = \delta T + \beta \delta T + p \delta v$$

where δv is the small amount the gas expands to prevent the pressure rising with the rise of temperature, and hence $p \delta v$ is the work done. We are supposing here that the gas is perfect, and are neglecting the gain of potential energy due to separation of the molecules. It would be quite easy to take account of it, but it increases the complexity of the equations, and only enters as a correction in the final result.

If we assume that the pressure of the gas is due to the impacts of small elastic molecules, we know that for unit mass $p v = \frac{2}{3} T$, so that with p constant $p \delta v = \frac{2}{3} \delta T$. Putting in this value and dividing the second equation by the first

$$\text{we get } \frac{C_p}{C_v} = \gamma = 1 + \frac{2}{3(1+\beta)}.$$

Hence if we know the ratio of the two specific heats of a gas we can calculate the relative rates of increase of the translational and the internal energy of the molecule. β is sometimes incorrectly described as being the proportion of the energy that is internal. This is not justifiable. All that β tells us is what proportion of a given increment of energy becomes internal, so that, when we find that β is zero for mercury vapour, we must not conclude that the molecule has no energy of rotation for instance, but only that under the circumstances under which γ was determined the rotation did not change appreciably as the temperature changed.

There are two principal methods used in the experimental determination of γ , Clément and Désormes' method, and Kundt's method, but as they are fully described in all the text-books it is unnecessary to go into much detail concerning them here.

In the former method the gas is slightly compressed in a large glass globe, and the pressure read. A stopcock is then opened for a moment to allow some of the gas to escape. The pressure falls rapidly, partly in consequence of the expansion alone, and partly because of the cooling caused by this expansion, and the lowest pressure reached is read quickly before the gas has had time to be warmed again by contact with the sides of the glass globe. The temperature then slowly rises, till it is the same as it was at the beginning of the experiment, when the pressure is read a third time. If it is assumed that the gas is perfect the ratio of the specific heats is given by the equation—

$$\gamma = \frac{\log p_1 - \log p_2}{\log p_1 - \log p_3}.$$

All who have used the method hitherto have made this assumption, and for some of the more permanent gases it leads to no appreciable error, but in most cases the equation is not accurate enough. Röntgen's value for the γ of carbon dioxide, for instance, would be raised about $\frac{1}{4}$ per cent. if a more accurate formula were used, and in the case of the more easily condensed gases and vapours the correction would be much greater.

It will be seen from the formula that the density of the gas need not be known. This is a great advantage of the method, for a small quantity of impurity only affects the result in so far as the impurity has not the same γ as the gas under investigation, and such an effect is very slight. Unfortunately the experimental difficulties are great. The vessel that holds the gas must have a capacity of 50 to 100 litres to avoid errors from conduction of heat through the walls, and gases are not easy to prepare pure in such large quantities. Further, no one has hitherto succeeded in devising a pressure gauge that is sensitive, dead-beat, and

free from elastic fatigue. If this could be done the method would probably be the best at our disposal.

Pringsheim has recently introduced a modification (*B. A. Rep.*, 1894) by reading the temperature immediately after opening the globe, instead of reading the pressure, using the resistance of a very thin strip of platinum as his temperature indicator. The modification seems to have improved the method considerably.

Kundt makes use of the fact that the square of the velocity of sound in a gas is approximately γ times the pressure divided by the density. The velocity of sound in the gas is deduced from its known value for air by causing the same note of high pitch to traverse two tubes, one filled with air, and the other with the gas under investigation, and observing the wave length of the sound in the two cases by means of fine dust spread along the tubes.

Here too a correction is required if the gas does not obey the laws of Boyle and Charles, but though this correction may reach as much as 2 or 3 per cent., it has been ignored by most investigators.¹

The method is probably the most accurate we have at present, as the conditions of accuracy have been very fully determined by its inventor, but it is seriously handicapped by the density of the gas appearing as a factor in the expression by which γ is calculated. This makes it necessary in most cases to determine the density experimentally, and renders the method very sensitive to small amounts of impurity in the gas.

A third method has been used by Müller (*Wied. Ann.*, 18, 1894) in a large number of observations, but as it assumes that alternate compressions and rarefactions of half a second period in a globe of glass holding only a litre are adiabatic, it must of necessity give inaccurate results, and need not be further described.

These three methods all require the amount of deviation of the gas from Boyle's law to be known before the calcula-

¹ The writer has given a formula and method of application that is accurate, and makes no assumption as to the form of the characteristic equation (*Phil. Trans.*, 185, p. 1).

tions can be made, which is a great disadvantage, for the shape of the isothermals is known for only a few gases, and the investigator is generally obliged to undertake a series of troublesome subsidiary determinations, if he wishes to secure accuracy. Jamin and Richard (*C. R.*, 71, 336) have devised a form of experiment that might be made independent of the density of the gas, or of its characteristic equation. A constant amount of gas is enclosed in a vessel, and has a definite quantity of heat given to it by means of a wire heated by an electric current, first at constant volume, and then at constant pressure. If, then, the rise of temperature is read in each case, the ratio of the two rises gives at once the ratio of the specific heats. Jamin and Richard in their experiments did not read the temperature directly, but when the volume was kept constant they read the increase of pressure, and when the pressure was constant they read the increase of volume, thus bringing in the old difficulty of knowing exactly how the pressure and volume depend on the temperature.

In practice the method is not likely to be accurate, for time must be given to allow the gas to come to a uniform temperature, and then heat will have been lost by communication to the walls of the vessel, and uncertain corrections will have to be introduced.

Considering the theoretical value of the constant γ , it is surprising that so few determinations have been made, and still more surprising is the extraordinary want of agreement among the results obtained by different observers for the same gas. The values found by any one observer are generally fairly consistent with each other, so that the experimental error appears to be small, but each form of apparatus seems to have a constant source of error of its own. This was especially marked in the case of experiments made with Clément and Désormes' apparatus before Röntgen showed that the size of the gas holder has a serious effect, if it is below a certain minimum. Kundt's apparatus has been largely used, and seems to be less subject to such one-sided errors, but when the subsidiary determinations of vapour density and isothermal curves are

made, the irregular errors cannot be kept much under 1 per cent. As was mentioned above, nearly all who have used the method have assumed the gases are perfect, and none but E. and L. Natanson and the writer have experimentally determined the density of the gases as they were used in the experiments, so that much of the work that has been done is of little value.

The table on p. 340 of the second edition of Landolt and Börnstein's tables gives an almost complete list of all the determinations that had been made up to 1893, with references. The experiments of Jamin and Richard mentioned above are omitted, as are also the writer's results, which have been published since the table was drawn up (*Phil. Trans.*, 185, 1, and *Nature*, p. 97, 7th March, 1895).

In Ostwald's *Zeitschrift* (12, 116) Petrini gives a very voluminous table containing not only the gases included in Landolt and Börnstein's table, but many others, whose γ 's he has calculated by an approximate formula from the determinations of C_p by Regnault and Wiedemann. From what has been said above, it is clear that it is little use trying to construct theories from such a table, for the values are so discordant that support could be found in it for almost any theory. A little time spent in consideration of the methods used and in consequent weeding out of results would have been well spent.

The following table contains what seem to the writer to be the best values of γ known at present. In most cases only three figures are given, and in many of these the third is probably only approximate. Four figures are given where the observer has used accurate equations.

THE RATIO OF THE SPECIFIC HEATS OF GASES. 279

Atomicity.	Name.	Formula.	γ
1	Mercury		1'67
	Argon		1'65
2	Hydrogen	H ₂	1'41
	Nitrogen	N ₂	1'41
	Carbon Monoxide	CO	1'40
	Hydrochloric Acid	H Cl	1'39
	Hydrobromic Acid	H Br	1'42
	Hydriodic Acid	HI	1'40
	Chlorine	Cl ₂	1'32
	Bromine	Br ₂	1'29
	Iodine	I ₂	1'29
	Iodine Chloride	I Cl	1'31
3	Carbon Dioxide	CO ₂	1'308
	Nitrous Oxide	N ₂ O	1'31
	Sulphuretted Hydrogen	S H ₂	1'340
	Carbon Bisulphide	C S ₂	1'239
4	Ammonia	N H ₃	1'30
5	Methane	C H ₄	1'313
	Methyl Chloride	CH ₃ Cl	1'279
	„ Bromide	CH ₃ Br	1'274
	„ Iodide	CH ₃ I	1'286
	Methylene Chloride	CH ₂ Cl ₂	1'219
	Chloroform	CH Cl ₃	1'154
	Carbon Tetrachloride	C Cl ₄	1'130
	Silicon Tetrachloride	Si Cl ₄	1'129
6	Ethylene	C ₂ H ₄	1'26
	Vinyl Bromide	C ₂ H ₃ Br	1'198
8	Ethane	C ₂ H ₆	1'18
	Ethyl Chloride	C ₂ H ₅ Cl	1'187
	„ Bromide	C ₂ H ₅ Br	1'188
	Ethylene Chloride	C ₂ H ₄ Cl ₂	1'137
	Ethylidene Chloride	C ₂ H ₄ Cl ₂	1'134
9	Allyl Chloride	C ₃ H ₅ Cl	1'137
	„ Bromide	C ₃ H ₅ Br	1'145
	Alcohol	C ₂ H ₅ OH	1'133
11	Propane	C ₃ H ₈	1'130
	Normal Propyl Chloride	C ₃ H ₇ Cl	1'126
	Isopropyl Chloride	C ₃ H ₇ Cl	1'127
	„ Bromide	C ₃ H ₇ Br	1'131
	Ethyl Formate	H COO C ₂ H ₅	1'124
	Methyl Acetate	CH ₃ COOCH ₃	1'137

During the past few months the interest of chemists and physicists has been specially drawn to the first two gases in this table, since it is on the observed value of the ratio of the specific heats that it is assumed that the gas argon is monatomic, and therefore elementary. The argument in favour of the monatomicity of the gas appears to be two-fold. On looking down the table it will be seen that, with the exception of gases with more than one halogen atom in the molecule, gases of the same atomicity show a decided tendency to have the same value for γ . Thus the diatomic gases are all near 1.4, the triatomic near 1.3, the pentatomic near 1.28, and so on. Admitting this as an empirical law, we conclude that argon has probably the same atomicity as mercury vapour, and mercury vapour is known from its chemical reactions and its vapour density to be monatomic. This argument receives support from another drawn from the actual value of γ . The values found in two experiments were 1.61 and 1.65, but these are probably both too low. In consequence of the difficulty of preparing the gas in large quantities, the experiments were made in tubes much narrower than the narrowest Kundt found could safely be used, and the effect of using too small a tube is to lower the velocity of sound, and hence to lower the observed value of γ . It is scarcely conceivable that the γ of any gas could be greater than 1.67, so we may conclude that argon has very nearly this value. Now, using the formula on p. 274 to calculate β , we find it comes out zero, so that when the gas is heated the energy given to it all takes the form of energy of translation of the molecule—there is none whatever taken up to give relative motion to the parts of the molecule. It does not, of course, follow that the molecule possesses no internal energy; all we can say is that if it has such energy, the circumstances under which the experiment was made were such that during the heating or cooling of the gas there was no change in the internal energy. If the molecule is anything more than a mere mathematical point it must be capable of rotation, but it is not unlikely that the energy of rotation would change more slowly than the energy of translation, as Watson (*Kinetic*

Theory of Gases, second edition, p. 49) and others have pointed out. It is generally assumed that the perfect elasticity of the molecules is a consequence of their not actually hitting each other in an encounter, but circling round each other under the influence of a mutual attraction or repulsion, like a comet round the sun. If the least distance between two molecules during an encounter is great compared with their size, the resultant force will pass approximately through the centre of mass of each, and very little energy of rotation will be communicated to either by the encounter, so that any appreciable change in the rotational energy may require a much longer time than the very small fraction of a second afforded by the sound waves used in Kundt's method.

The important question, however, is whether a polyatomic gas can have β equal to zero. It is difficult to believe that this could be the case, when of the forty certainly polyatomic gases whose γ 's are known not one has a value of β anything approaching zero. With the exception of mercury, β is least for the diatomic gases, but even here it is .67, and for the gases of higher atomicity it reaches 3 or 4. The greater the complexity of the molecule the greater is the internal energy, and for no capacity for internal energy we seem to be driven to assume the simplest possible molecule—a single atom.

After all, in our present state of ignorance regarding the status of the atom in the molecule, the argument is little more than an argument from analogy. Such an argument is the stronger, the greater the number of points of agreement between the two objects or phenomena compared, and the fewer the points of disagreement. The question at issue seems to be just the sort of case where the argument may break down, for argon differs in such a remarkable way from all other known substances that it would be unsafe to deny the possibility of further eccentricities in the dynamics of its molecule. Consider the diatomic gases in the table. Six of them have γ near 1.41, and hence β near .67—four have γ near 1.3, and hence β near 1.2. If such a large range as this is possible with

gases of the same atomicity, may there not be another class of diatomic gases possible with β zero, or very small?

It has already been mentioned that, throughout the table, gases with the same atomicity have in most cases the same γ , but there is one class of gases that uniformly prove exceptions. These are the gases with more than one halogen atom in the molecule. Their proving an exception cannot be due to the halogens having intrinsically a higher heat capacity than other atoms, for in several cases, such as H_2 , C_2H_6 and C_3H_8 , one H can be replaced by Cl without change in γ , and the natural conclusion to draw from this is that the Cl has itself the same heat capacity as the H that it replaces. We seem, in fact, to have in the case of gases something similar to Dulong and Petit's law of equality of atomic heats for elementary solids, but the divergences cannot be explained in the way in which the anomalous values for carbon, etc., were explained, for chlorine, for instance, was shown by Strecker to have a value of γ that does not vary with the temperature.

Since then the number and nature of the atoms in the molecule do not fix the value of γ , we must probably look to their relations to each other or the configuration as an important element, and from the many cases where atoms of different kinds are interchangeable without altering γ , it may very well be that the distribution of energy depends on nothing but the configuration. Of course the term configuration must be taken to include the size as well as shape, otherwise we should have no explanation of the difference between H Cl and Cl_2 , for in a diatomic molecule the atoms must simply lie side by side, and no variation in shape is possible. On this hypothesis the atoms in the chlorine molecule would be farther apart than the atoms in most diatomic molecules. Also methyl chloride would have to be taken as having a different configuration from methane. Chemical facts tell us that we can get but one CH_3Cl whichever H in CH_4 we replace by Cl, but this does not preclude the possibility of the chlorine distorting the molecule to a shape that is the same in every case.

We might go a step farther still, and ask whether the

peculiar relation of the two chlorine atoms to each other when they come in the same molecule is not a result of their being no longer monovalent, but is—according to the most reasonable theory of valency, the electrical theory—the result of their carrying more than one unit of electricity each.

These are mere speculations at present, but they serve to show the kind of information that may be got by further determinations of the ratios of the specific heats of suitably chosen compounds. It would be interesting, for instance, to investigate a number of compounds containing well-marked radicles, such as NH_2 or OH , to find whether the radicle always contributes the same amount to β , and also to find whether it is a general law that isomers have the same γ .

Except for the difficulty in making the determination γ might be expected to be as serviceable in fixing constitutions as the numerous constants, index of refraction, surface tension, etc., already largely used for the purpose by organic chemists.

An interesting piece of work has been done on nitrogen peroxide by E. and L. Natanson. These physicists determined the ratio of the specific heats over a long range of pressures, simultaneously making careful determinations of the density. They found that at the highest pressure used, when according to the usual theory 15 per cent. of the gas was dissociated into NO_2 , γ had the value 1.17, which is near the average value for a six atom molecule; whilst, when the gas was fully dissociated, the value of γ was 1.31, about the same as has been found for most three atom molecules, thus showing conclusively that the gas is really dissociating, and that the variation in density is not merely an abnormal case of the usual deviation from Boyle's law.

The effect of change of temperature on γ has not received the attention it deserves. Several observers, notably Wüllner and Strecker, have looked for a dependence of γ on the temperature, but no one has ever found it except Wüllner, who found that the γ 's of carbon dioxide, carbon monoxide, nitrous oxide, ethylene and ammonia all fell as the temperature rose, in some cases by

as much as 4 per cent. between 0° and 100° . Strecker, on the other hand, found no certain change for the halogens and their hydracids up to 400° . From the arrangement of Wüllner's apparatus it is difficult to believe that the gases really had as high a temperature as he attributed to them, and the result needs confirmation.

Neither Strecker nor Wüllner took account of the deviation of the gases from Boyle's law, but this would not account for anything like so great a change as Wüllner found, and in any case hydriodic acid, which showed no change, deviates far more widely than carbon monoxide, which changed considerably.

A repetition of the experiments on carbon dioxide, for instance, would be of value. The observations should not be made merely at 0° and 100° , but at intervals over as long a range as possible, in order to see whether the value of γ approaches asymptotically to an intelligible limit. If Wüllner's results prove to be substantially correct, the question arises why some gases vary with the temperature and others do not, and opens up a large field for research.

Any discussion of the ratio of the specific heats would be incomplete without reference to a theorem that has attracted considerable attention lately—Boltzmann's theorem on the partition of energy in a dynamical system. We shall consider here only the physical side of the theorem, as the mathematical arguments for and against it have already been discussed in this journal by Mr. H. S. Burbury; but before stating the theorem it will be necessary, for the benefit of non-mathematical readers, to explain briefly what is meant by "degrees of freedom," a term that will be frequently used.

By the number of degrees of freedom of a system is meant the minimum number of co-ordinates—lengths, angles, etc.—necessary to specify completely the position and configuration of the system.

As an illustration take the case of a ship at sea. The locality of the ship cannot be fixed by less than two co-ordinates; its latitude and longitude are the two usually chosen, though other pairs would do equally well. Next

we require to know how the ship's head is pointing. This is usually defined by reference to the points of the compass, but we might more simply state the angle the ship's head makes with some fixed line, say the N. and S. line. Finally, it may be a matter of interest to know whether the ship is heeled over, and whether the line joining the bow and stern is tilted up or not. For this purpose we require two more co-ordinates, say the angle the plane through the masts makes with the vertical plane, and the angle a line along the deck from stem to stern makes with the horizontal plane. If the ship is a rigid body, so that its parts do not move relatively to one another, and if the sea is waveless, so that the centre of gravity of the ship does not move up or down, the position will be completely fixed by these five co-ordinates, and cannot be fixed by any smaller number than five, however they may be chosen. Moreover, a moment's consideration will show that the ship can be moved in such a way as to alter any one of these co-ordinates without change in any of the others—hence the name, degrees of freedom.

If we were defining the position of a balloon instead of a ship, we should need to know its height above the earth in addition to the five co-ordinates already given, so that a rigid body free to move in any direction, and to rotate in any way, has six degrees of freedom.

Each of these co-ordinates may at any moment be changing, so that corresponding to each co-ordinate will be a rate of change or velocity, and if we know all the co-ordinates and all the corresponding velocities at any moment, the position and motion of the body or system will be completely specified.

The most general conception of the constitution of a gas is to regard it as made up of a number of molecules, each of which is a dynamical system with a definite number, say q , degrees of freedom.

Three of these fix the position of the centre of gravity, and the remaining $q - 3$ show how the parts of the molecule are arranged at any moment with reference to the centre of gravity.

The total kinetic energy of the molecule can be divided into two parts, namely, the kinetic energy it would have if its mass were all concentrated at its centre of gravity, and were moving with the velocity the centre of gravity actually has ; and the kinetic energy due to the motion of the parts of the molecule relatively to the centre of gravity. The first is $\frac{1}{2} m (u^2 + v^2 + w^2)$, where u , v and w are the components of the velocity of the centre of gravity in three directions at right angles, and contains none of the other velocities in its expression. The second part is a homogeneous function of the second degree of the rates of change of the remaining $q-3$ co-ordinates. *Whenever the kinetic energy of each of a large number of similar colliding systems can be divided in this way, so that one part of the expression contains none of the velocities corresponding to n of the q co-ordinates, and the other part none of the remaining $q-n$, Boltzmann's theorem states that the average value of the first expression taken over a large number of systems is to the average value of the second as $q-n$ is to n ; or more shortly but less accurately, the average value of the kinetic energies of two parts of the system is in the ratio of the number of degrees of freedom of the two parts.*

The special application to the molecule of a gas then would be that, if the molecule has q degrees of freedom, the average kinetic energy of the motion of translation of the system is to the average kinetic energy of the internal motions in the ratio of 3 to $q-3$.

Hence if the number of degrees of freedom is the same at all temperatures, the rates of increase of these two forms of energy when the temperature rises must be in the ratio of 3 to $q-3$, or $\beta = \frac{q-3}{3}$, so that from the ratio of the specific heats we could calculate the number of degrees of freedom of the molecule.

The theorem has by no means been allowed to pass without criticism, attacks having been very freely made on it both from the mathematical and the experimental side. As regards the mathematical criticisms it is sufficient to say that the balance of opinion among mathematicians appears

to be in favour of the theorem as a question of abstract dynamics. The difficulty lies in its application.

The physical objections are serious, but perhaps not insuperable. Let us consider the one most often quoted.

Mercury has a very brilliant spectrum consisting of a large number of lines. The vibrations of the ether that give rise to this spectrum are presumably caused by the motion of something or other within the molecule.

Every separate motion in the molecule implies at least one degree of freedom, so that the value of q for mercury should be very large. Hence β should be large, and γ very little greater than unity, meaning that when heat is communicated to mercury vapour nearly all the energy should go into internal motions of the molecules, and very little to increase the kinetic energy of translation of the molecules, that is, the temperature. But we know from Kundt and Warburg's experiments that β is zero for mercury vapour, or none of the energy communicated to the gas takes the form of internal vibrations.

This seems conclusive against the theorem if the degrees of freedom involved in the production of spectra are really independent dynamical degrees of freedom at all. Boltzmann, however, suggests (*Nature*, 28th Feb., 1895) that the mercury molecule is only indirectly concerned in the production of the spectrum; that it is the ether which has a structure, and the numerous degrees of freedom belong to it, and not to the molecule. Schuster (*Nature*, 24th Jan., 1894) and Watson (*Nature*, 3rd Jan., 1895) have also suggested possible ways of reconciling the existence of a complicated spectrum with observed values of γ .

It should be noticed that so far as experimental evidence goes at present, a gas can probably not be made to give a line spectrum by mere heating. Wherever we have such a spectrum produced, there is some electrical or chemical action going on,¹ so that in the absence of evidence to the contrary, it may be inferred that the vibrations in the molecule which cause the spectra are not heat effects—

¹ Much work has been done on the subject recently by Pringsheim, Paschen, Smithells and others, but the question is still under discussion.

they are of such a nature as not to be capable of being excited by collisions between the molecules; and hence for some reason as yet not understood they are removed from the sphere of Boltzmann's theorem.

It has been objected again that, even if the mercury molecule is not capable of vibrations, it must at least be a rigid body, and so have six degrees of freedom, whilst Boltzmann's theorem only allows it three. Watson's suggestion quoted above seems to be a sufficient answer to this. Boltzmann's theorem only tells us what the distribution of energy is *when the gas has reached a steady state*, and it may very well be that with the rapid change of temperature caused by the passage of sound waves the gas never has time to reach the steady state.

Possibly the values of γ might be very different if the changes of temperatures were much slower than they are in Kundt's method. The accepted value of γ for carbon dioxide obtained by Kundt's method is about 1.3. Regnault's value for C_p between 15° and 100° is .2025. Joly's value for C_v between 12° and 100° is .1653, and the ratio of these is 1.22. Both C_p and C_v are difficult to measure accurately, but 7 per cent. seems to be too much to attribute to experimental error. It would seem that we have here to do with forms of vibration that only take their share of the energy when given more time than is afforded by sound vibrations.

For the majority of diatomic gases γ is near 1.4, thus pointing to five degrees of freedom. This again is less than the number possessed by a single rigid body. If we ascribe three to the linear motion of the centre of gravity, we have left only two for the internal motions, which is not enough to allow the molecule to rotate in the most general way. The molecule has, in fact, the same number of degrees of freedom as a finite material *line* moving freely in space. If the two atoms were small compared with the distance between them, the rotation about the line joining them would probably change much more slowly than the rotation about any line perpendicular to this line, and the molecule would appear to have only five degrees of freedom.

Chlorine, bromine, iodine and iodine chloride, though diatomic, have γ near 1.3, and hence eight degrees of freedom. This is only one instance of what, as was said above, holds generally. Two halogen atoms together in one molecule invariably give a low value to γ , and hence, according to Boltzmann, an abnormally large number of degrees of freedom. What this means it is impossible at present to say.

With regard to the polyatomic gases it is sufficient to say that, with the exception of those with more than one halogen atom in the molecule, nearly all have a value of γ that makes β approximately equal to $\frac{1}{3}n$, where n is the number of atoms in the molecule. The relation is only roughly approximate, the divergences being in many cases too great to be accounted for by errors of observation. Calculating the number of degrees of freedom from this result we find that we have, in addition to the three required by the motion of translation, approximately one for each atom in the molecule.

It is an interesting task to devise modes of vibration that satisfy this relation, but the possibilities with gases of high atomicity are too numerous to give much scientific value to the work.

There is one very striking feature in the table on p. 279, and that is the absence of any gases with values of γ between 1.67 and 1.41. This is a strong argument in favour of the dynamical theory of gases in general, and Boltzmann's theorem in particular. The former value of γ gives $q = 3$, and the latter gives $q = 5$, both of which, as we have seen, are quite intelligible; but what would be done with a gas whose γ was 1.5, and whose molecule had consequently *four* degrees of freedom? Such a gas would be very hard to reconcile with our present notions, and if ever discovered would bring about a profound change in the hypothesis of molecular physics.

J. W. CAPSTICK.

PROGRESS IN PHYSICAL CHEMISTRY DURING 1894.

PART II.

MIXTURES.

LIQUIDS.—In connection with the physical properties of mixed liquids, Ramsay and Aston (73) have determined the surface tension of four binary mixtures of non-associated liquids. In the case of mixtures of toluene with piperidine, and benzene with carbon tetrachloride, the surface tension and the molecular surface energy are practically the mean of those of the constituents. The simple admixture rule is not obeyed, however, by mixtures of chlorobenzene with ethylene dibromide, and carbon bisulphide with chloroform. From the rate of change of the molecular surface energy, the authors infer that in all cases, but the last, no change in the molecular aggregation of the liquids is produced by admixture.

As another means of obtaining evidence regarding change in molecular complexity produced by admixture, Paternò and Montemartini (74) determine the densities of mixtures of benzene with liquids which, from freezing-point observations, have abnormally high molecular weights when dissolved in benzene. They find that on adding one of the lower fatty alcohols or acetic acid to benzene expansion occurs. This, they consider, is an indication of disaggregation, and, therefore, of the existence of molecular aggregates in the liquids. On the other hand, according to surface-energy measurements, although chlorobenzene and ethylene dibromide expand on admixture there is no molecular aggregation. Indeed, that density observations are not well suited for the end in view is shown by the fact that the authors find that benzyl alcohol and butyric acid, which have high molecular weights so far as freezing-point observations go, exhibit contraction when added to benzene.

Solids.—A good deal of work has been done on the fusibility of mixtures of solids. If crystallisation be instituted in a fused mixture of two isomorphous salts, the crystals which begin to separate consist of both of the salts present, and not of one of them only, as is the case with ordinary mixtures. For this reason, on plotting the freezing-point and composition of isomorphous mixtures in a co-ordinate system, the curve is continuous and does not consist, as in the ordinary case, of different parts which correspond with the different salts which separate on freezing. In a paper by Le Chatelier (75) this rule was apparently disobeyed, but Küster (76) has shown that several of the pairs of salts used were not truly isomorphous, and in a later paper Le Chatelier (77) obtains curves for isomorphous carbonates which conform to the rule. That this point should be satisfactorily settled is important, for in observations of the freezing-point, we have evidently a means of detecting isomorphism.

Observations on the melting-point may also be used to detect the formation of a double compound. The freezing-point curve of an ordinary binary mixture, plotted as above described, shows a minimum corresponding with the eutectic mixture. If, however, a double compound be formed the curve will exhibit a maximum corresponding with the double compound, and two minima corresponding with the eutectic mixtures of the double compound with each of its constituents. In this way Le Chatelier (78) concludes that a double compound is formed in the case of lithium and potassium carbonates.

In a similar way from the freezing-point of triple alloys, Heycock and Neville (79) infer that the compound Au Cd exists in solutions where the solvent may be tin, bismuth, thallium, or lead. There is also evidence that Ag_2Cd is formed in solutions in lead, tin, and thallium. Gold and aluminium when dissolved in tin form the stable insoluble compound Au Al_2 . Laurie (80) has also tried to show the presence of compounds in alloys by observations on electromotive force. His method may thus be illustrated. If a plate of copper and another made partly of zinc and

partly of copper be immersed in a solution, the observed E. M. F. is that between copper and zinc. If the zinc in the composite plate were finely divided and mixed with the copper it may be assumed that the result would be the same. If, however, the zinc combined with the copper, the E. M. F. would be that between the compound and copper. Consequently, if we keep on adding zinc to the copper, and a compound is formed, a point will eventually be reached at which the copper is saturated, and free zinc will then be present in the plate. When this happens there will be an abrupt rise in the E. M. F., for it will now be that between copper and zinc, and the composition corresponding with the rise will be that of the compound of copper and zinc. In this way the author has previously inferred that Cu Zn_2 and $\text{Cu}_3 \text{Sn}$ exist, and he now finds (80) that his observations lead to the same results as measurements of electrical resistance in the case of the alloys examined by Mathiessen. Using alloys of the metal-pairs, Bi-Sn, Bi-Pb, Bi-Zn, Bi-Au, Bi-Ag, Au-Ag, Cd-Zn, Sb-Sn, and Sb-Pb, in the last case alone was there evidence of combination. Ostwald (81) has pointed out that these observations would be more valuable if more attention had been paid to the composition of the solutions in which the alloys were immersed, because the E. M. F. depends on the concentration in the solution of the ion of the metal plate, and from the mode in which the experiments were made different amounts of metal might have dissolved in the solutions in different cases.

According to Haas (82), the copper-zinc alloy, which has the maximum specific resistance, has the composition expressed by $\text{Cu}_2 \text{Zn}$. Since alloys containing from 47 to 99 per cent. of copper could not be drawn into wire, the author was unable to test by this method the existence of Laurie's Cu Zn_3 alloy. It is to be hoped that efforts will soon be made to see whether these different methods lead to the same results, for in the present state of the theory of solids such agreement would constitute the strongest proof of their validity.

Wiesengrund (83) has tried to show that the lead-tin

alloy, which, as regards its density, gives the largest exception from the admixture rule, has also the lowest melting-point, and has the approximate composition Pb Sn_3 . This result differs from those of previous observers. Paternò and Montemartini (84) also assert that certain eutectic mixtures have a definite chemical composition. They find, for example, that mixtures containing one molecular proportion of paraxylene to two of acetic acid, or one of paraxylene to three of trimethyl-carbinol, are eutectic, and they conclude that these results throw light on the existence of molecular aggregates in solution. It has to be stated, however, that the existence of eutectic mixtures can readily be explained without the assumption of chemical combination.

A curious point regarding the structure of isomorphous mixed crystals has been noticed by Ambron and Le Blanc (85). Mixed crystals of lead and barium nitrates were doubly-refracting. On treating them with a saturated solution of barium nitrate the lead nitrate was dissolved out, but a skeleton remained, which consisted of regularly arranged particles of barium nitrate of about 0.03 mm. side, and the double refraction had disappeared. From these and other experiments it appears that the constituents of a mixed crystal are in a state of rough, mechanical mixture, and not in a state of molecular admixture as has been commonly supposed.

Muthmann and Kuntze (86) have determined the solubility in water of three pairs of isomorphous salts, namely, mono-potassium phosphate and arseniate, potassium chlorate and permanganate, and potassium and rubidium permanganates. The curves showing how the amount of one constituent present in the solution varies with its amount in the mixed crystal are very different in each case, the noteworthy point being that they correspond with Roozeboom's predictions (87), based upon the analogy between the solubility of mixed crystals and the evaporation of mixed liquids.

SOLUTIONS.

An interesting lecture (87) on the origin of the new theory of dilute solutions, and dealing also with the present position of the theory, was delivered by van't Hoff to the German Chemical Society early in 1894. In it he makes clear how he was able by means of the work of Pfeffer and De Vries, that is, by means of the conceptions of osmotic pressure and semi-permeable partitions, to correlate the different properties of dilute solutions by the application of thermodynamical principles, and how the *facts* of the case showed that solutions obeyed laws identical with those of gases. It is also clearly pointed out that these laws do not constitute a theory of solutions. The theory of solutions begins, according to van't Hoff, when the exceptions to the above simple laws, those, say, of electrolytic solutions, are interpreted as being of a secondary nature. This is obviously the rational view of the matter, for it is only when attempts are made to fix the molecular state of dissolved substances that anything of a hypothetical nature is introduced. An important paper bearing on this question of molecular state has been brought forward by Duhem (88), who gives a formal proof of the theorem that every formula obtained by the application of thermodynamical considerations alone to a mixture or solution remains the same, no matter what assumptions be made regarding the molecular condition of the substances. It follows, therefore, that thermodynamics alone cannot decide whether dissolution is attended by change chemical or otherwise in the molecular state of the dissolved substance.

Osmotic pressure.—An attempt to throw light upon the action of semi-permeable membranes has been made by Ramsay (89). A platinum vessel connected with a manometer, and containing nitrogen, carbon dioxide, carbon monoxide, or cyanogen, was closed by a palladium plate and immersed in hydrogen, or hydrogen mixed with other gases, the temperature being kept constant, generally at about 280° . Since palladium acts as semi-permeable membrane, allowing hydrogen to traverse it, the question was: Would the pressure of the hydrogen inside and outside

the vessel eventually become the same? In all cases this was nearly but not quite the case, the ratio of the inside to the outside pressure varying between 0.9 and 0.97. In the same direction Moore (90) has put forward the view that osmotic pressure may be due to differences between the capillary pressures of solvent and solution acting through pores of molecular dimensions in the semi-permeable wall. Ostwald points out, however (91), that as solvent and solution are miscible with one another, there is no surface of separation between them, and consequently that capillary action in the ordinary sense is impossible.

For some time past a discussion (92) has been going on regarding the validity of Arrhenius' deduction from theory that the osmotic pressure of a dilute aqueous solution is proportional to the lowering of the freezing-point. Dieterici by using Fischer's numbers for the vapour-pressure of ice and water found this was not strictly true, but Arrhenius by means of Juhlin's more recent observations showed that the proportionality was valid within the limits of experimental error, and Dieterici has admitted that for depressions of the freezing-point up to 10° this is the case.

In his last paper, Dieterici gives a relationship between osmotic pressure and depression of the freezing-point which applies to concentrated solutions. Ewan (93) has also dealt with strong solutions. He finds that the depression of the freezing-point of a non-electrolyte will be greater than van't Hoff's theory of dilute solutions demands if the heat of dilution be positive and *vice versa*. The observed depressions of the freezing-point of cane sugar and those calculated by this formula agree but approximately. A similar and detailed inquiry dealing with the properties of electrolytic solutions of finite concentration has been published by van Laar (94).

As regards molecular weight estimations by means of osmotic pressure, it may be noted that Lob (95) has described a method employing red blood corpuscles. A small quantity of blood is added to the solution and the flask containing them is rapidly rotated for three minutes,

and the colour of the supernatant liquid is then noted. Two solutions which are just coloured after this treatment have the same molecular concentration, and hence if the molecular weight of one of the dissolved substances is known that of the other can be calculated. The method is rapid, but cannot be used for acids and bases. In carrying out the method of De Vries, Schreiber (96) finds that the peduncle of the dandelion affords good material, and according to Hamburger (97) by the method of De Vries the same results are obtained for the osmotic pressure of solutions of albumen as by the methods depending on red blood corpuscles or depression of the freezing-point.

Vapour pressure and boiling-point.—Besides the work of van Laar, already referred to (94), that of Ewan (93) contains a theoretical deduction of the vapour-pressure formula of a strong solution. Ewan shows that the vapour pressures of sulphuric acid solutions calculated by his expression from the freezing-point and heat of dilution, accord with the facts.

A modification of Beckmann's boiling-point apparatus for determining molecular weights has been described by Linebarger (98). This and the numerous other forms of apparatus which have been proposed, together with the various improvements in the accessories of the boiling-point apparatus, are fully discussed by Beckmann in a recent paper (99), in which he describes what he regards as the most suitable type. Gernhardt (100) has proposed to replace the platinum wire fused through the base of the boiling-point flask by a less costly piece of red Jena glass.

From the boiling-point of alcoholic solutions, Müller (101) finds that ferric chloride has the formula Fe Cl_3 . In ethereal solution the molecular weight diminished with the dilution from 200 to 151, the theoretical value for Fe Cl_3 is 162.5.

Kruss and Thiele (102) from the boiling-point of solutions in ether, benzene, chloroform and carbon bisulphide, and from the freezing-point of solutions in benzene and acetic acid, conclude that in these solvents iodine has the formula I_2 . The difference in the colours of the solutions is, there-

fore, no direct indication of the molecular state of the iodine. They also made observations of the absorption spectra of solutions in 34 solvents, and in order to explain the results assume with Anschütz and Behrend that molecular complexes $(I_2)_n$ are formed, the individual molecules of which exert an independent effect on the boiling-point and freezing-point, but behave as a complex as regards the colour of the solution.

In the case of electrolytic solutions, sufficient work has now been done to prove that although in aqueous solutions the electrolytic dissociation as deduced from the boiling-point agrees with that deduced from the conductivity, this is not so in alcoholic solutions. Schlamp's work (103) on solutions in water and propyl alcohol, and the work of Woelfer (104) together with that mentioned on p. 300 make this point clear. Of course it has to be noticed that the conductivity is generally measured at the ordinary temperature, and the dissociation may be less at the boiling-point. Ostwald (105) thinks, however, that some cause is operative which tends to make the result obtained from the boiling-point too small; whether or not it is molecular aggregation of undissociated molecules is at present unknown. It is noteworthy that Woelfer finds contrary to Raoult's observations that in alcoholic solution the molecular weights of certain salts are not normal, but too small, and become smaller with the dilution as the dissociation hypothesis demands.

Freezing-point.—The validity of the methods in use for determining the freezing-point has been the subject of a somewhat heated controversy (106).

H. C. Jones and Loomis each described a method in which the thermometer was read to the $1/10,000$ th of a degree, but their results in general differed considerably. F. Kohlrausch suggested that the discrepancies might be due to errors in Jones' method, particularly in connection with his thermometer, the bulb of which contained over 200 gr. of mercury. To this Jones replied that his results were in harmony with those deduced from observations on conductivity, and suggested that the substances used by

Loomis were not quite pure. Pickering also criticised Jones' method, and showed that the character of the results indicated that the thermometer used had not been properly calibrated. In answer, Jones has stated that his thermometer was calibrated, and that he considered the results of different observers were not the same because each obtained but an approximate value for the freezing-point, since the actual temperature at which solid solvent and solution are in equilibrium cannot be determined by the ordinary method.

To Nernst and Abegg (107) belongs the credit of first obtaining definite evidence as to how the discrepancies arose. They show theoretically and practically that in ordinary cases the observed freezing-point is a function of the apparatus used, the rate of stirring, the temperature of the cooling bath, etc. By keeping the temperature of the cooling bath constant and stirring at a constant rate they show how to find approximately the corrections necessary to obtain the true freezing-point. Their experiments prove that by altering the conditions of experiment, values varying between 1.6 and 2.1, that is, by 25 per cent., could be obtained for the molecular depression of a 1 per cent. solution of sugar, but on applying the corrections deduced by their method all these results gave practically the value demanded by theory, namely, 1.87. They also make it clear that even when the corrections are used it is quite useless to attempt to measure the depressions nearer than the $1/10000$ th of a degree.

A new method applicable to the case of very dilute solutions has been described by Lewis (108). By its use Wildermann (109) has verified van't Hoff's law of the depression of the freezing-point in the case of aqueous solutions of sugar, urea, and alcohol; he also shows that the degree of electrolytic dissociation calculated from the freezing-point of solutions of potassium chloride and sulphuric, trichloroacetic, dichloroacetic, and nitro-benzoic acids agrees with that calculated from the conductivity; and finds that the dissociation of the last two acids obeys Ostwald's dilution law.

Ponsot (110) describes another method, in which he adds pounded ice to the solution, finds the temperature when equilibrium is attained, pours off the solution and determines its concentration by analysis.

Two new solvents have been added to the list. Paternò and Montemartini (111) show that paraxylene has a molecular depression of 43. The majority of substances when dissolved in it give normal molecular weights, hydroxy compounds, just as in the case of benzene, being exceptions. According to Lespieau (112) the hydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ melts at 8.53° and behaves as a solvent with a definite molecular depression of 48.

Noyes and Whitney (113) find that in aqueous solution alkaline aluminates have the formula M Al O_2 . Borates have a similar formula unless excess of boric acid be present when acid salts are formed.

The behaviour of solutions in benzene of some 80 oxy-compounds has been studied by Auwers (114). If the molecular weight in solutions of medium concentration is abnormally large, he concludes that the substance is a hydroxy compound. Certain derivatives of acetoacetic acid, diacetylacetone, and the oxy-methylene ketones appeared to be ketonic; the acid derivatives of the primary organic bases gave abnormal molecular weights, but the secondary and tertiary compounds gave normal values. Mercaptans differ from the alcohols in showing no aggregation. (Compare pp. 227, 228 and 234.) From the depression of the freezing-point of acetic acid by water in presence of sulphuric acid, H. C. Jones (115) obtained evidence of the existence under the experimental conditions of the hydrates $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$. Similar observations gave no indication that water and alcohol combine, but action of some kind seemed to be exerted by water on sodium acetate.

Conductivity.—In a lengthy paper, which is practically a review of present knowledge of ion migration, Bredig (116) calculates from conductivity observations the velocities of some 300 different ions. He finds that the velocity of elementary ions is a periodic function of the atomic weight.

Isomeric ions of analogous constitution have almost the same velocities. If the weight of an ion be increased by equal increments, the velocity is diminished by amounts which become smaller and smaller. In general a retarding effect is produced on replacing H by Cl, Br, I, Me, NH_2 or NO_2 ; or on replacing N by P, As, or Sb; or S by Se or Te. Retardation also occurs if monamines be converted into diamines, or dicarboxylic acids into monocarboxylic acids, etc. Constitution often exerts a marked influence; of metameric ions the most symmetrical travels fastest. There can be no question, therefore, of the closeness of the relation which exists between the ionic velocity and the chemical nature of the ion.

The influence of the nature of the solvent on the conductivity has been investigated by Völlmer (117), who uses solutions in water, methyl alcohol and ethyl alcohol. In general the conductivity increases with the dilution, and approaches a limit. If the limiting value for water be taken as 1, in the case of methyl alcohol it is 0.73, and in the case of ethyl alcohol 0.34. In very dilute solutions the temperature coefficient of the conductivity is practically the same as that of the viscosity coefficient of the solvent. Ostwald's dilution law does not apply, and the author finds in accord with other observers (see p. 297) that the boiling-point of an alcoholic solution cannot be calculated from the conductivity. Intimately related to these observations are those of Kawalki (118) on the diffusion of salts in alcohol. The diffusion coefficient is not quite constant, but increases with the dilution. The important point, however, is that at any concentration the ratio of the diffusion coefficients in water and alcohol is practically the same as that of the conductivities at infinite dilution. The rate of movement of the ions in water is therefore about three times as fast as in alcohol, and the results in the main support the dissociation theory.

Wildermann (119) shows that the order of the dissociation of acetic acid and certain of its derivatives is the same in alcohol as in water, and Campetti (120) finds that the transference numbers of lithium chloride and silver

nitrate are almost the same in water and alcohol, but as this is not the case for water and methyl alcohol he regards the transference ratio as a function of the solvent.

One of the most interesting questions in connection with conductivity is : Why should certain solvents only give solutions which readily transmit the current ? In answer to this question, Nernst points out that if the ions be electrified points the forces between them will be diminished the higher the dielectric constant of the medium, and hence the dissociation should be greatest for solvents having the largest dielectric constant. The dissociation of hydrogen chloride in hydrocarbons, ether, isobutyl alcohol, ethyl alcohol, methyl alcohol and water, is shown to obey this rule, water having by far the largest dielectric constant. This action of the solvent was pointed out by J. J. Thomson in 1893, and Whetham (122) has shown that the behaviour of solutions in water, methyl alcohol and ethyl alcohol agrees quantitatively with the theory if corrections are introduced for the viscosities of the solvents.

Many observations on solutions point to the fact that water is, to an extremely slight extent, dissociated into ions, and the amount of the dissociation has been calculated in various ways (123). The simplest method makes use of Kohlrausch's numbers for the conductivity of water. This calculation was made by Ostwald, who, by means of Nernst's theory, also obtained an independent value from the electromotive force of a voltaic cell with electrodes reversible as regards hydrogen ions. Ostwald's new value has recently been slightly modified by Nernst.

Arrhenius by using Shields' results for the hydrolysis of sodium acetate by water, and Wijs from the velocity of saponification of methyl acetate by water, have also obtained measures of the dissociation, and Laar has tried to show theoretically that Wijs' value is most probably correct. The numbers thus obtained are as follows :—

Kohlrausch,	$<0.6 \times 10^{-6}$ at 25° .
Ostwald—Nernst,	0.8×10^{-7} at 18° .
Arrhenius—Shields,	1.1×10^{-7} at 25° .
Wijs,	1.2×10^{-7} at 25° .

The specific conductivity of the sample of water from which Kohlrausch's value was obtained was 0.25×10^{-10} at 18° . Recently Kohlrausch and Heydweiller (124) have shown more clearly than ever to what a large extent the conductivity is affected by the merest traces of impurity. From observations on samples of different degrees of purity, one of which was the purest yet obtained, they calculated, after making use of the views of the new theory of solutions, that the conductivity of pure water was only 0.0361×10^{-10} . The dissociation deduced from this number is:—

$$1.05 \times 10^{-7} \text{ at } 25^\circ.$$

It is certainly surprising, considering the extreme smallness of the amount, that all these methods indicate that at 25° every 10 million litres of pure water contain about 1 gram of hydrogen ions.

Two curious points arise in a paper by Daniell (125). If a sufficiently thin metallic partition be placed in a voltameter when the current passes no gas is evolved at the partition. The critical thickness for gold is 0.09 mm., and for aluminium 0.035 mm. In the case of a copper sulphate solution the salt itself, and not the copper ions, appears to traverse a gold leaf partition.

Observations on conductivity are now largely used in determining the constitution of organic acids. It is noteworthy that Werner and Miolati (126) have attempted to use the same method to throw light on the structure of the complex double salts of ammonium and platinum, cobalt, etc.

Optical properties.—Most of the work on optical properties may be grouped around the dissociation hypothesis. From observations on the refractive index of aqueous solutions, Hallwachs (127) and Bary (128) find there is no evidence of dissociation. It is to be noted, however, that this result is not surprising as the dissociation of the substances used varies little over the changes in concentration studied. According to Muynck (129) the refractive index of solutions of salts containing iodine gives no proof of the presence of the double and triple molecules indicated by Hittorf's transference ratios.

The rotatory powers of salts of α -bromcamphoric acid when equally dissociated are found by Walden to be the same (130); if two active ions be present the rotatory power is found to be the sum of the rotatory powers of each. Carrara (131) also shows that the rotation of salts of nicotine conforms to the dissociation theory, and more striking support still is furnished by Blossfeld (132). If an equivalent of a strong acid be added to a solution containing an equivalent of asparagine, the rotation is altered to about the same extent no matter what acid be used; this is no longer true, however, with weak acids. The explanation is that the strong acids form salts which are not hydrolysed and are almost completely dissociated; the rotation in equivalent solutions is, therefore, due to the same number of active ions and is the same for all. With weak acids hydrolysis occurs, and the dissociation and hence the rotation varies in each case.

The rotation of rhamnose in isopropyl alcohol is positive but is negative in ethyl alcohol. From observations on the boiling-point, Sale (133) finds that in ethyl alcohol the molecular weight is too high.

The rotations of solutions in chloroform of position isomers, chiefly derivatives of phenyl carbamic acid, show, according to Goldschmidt and Freund (134), that in general the value of the meta-compound is intermediate to those of its ortho- and para-isomers. Kannonikoff (134) has tried to prove experimentally that α , the angle of rotation in a 200 mm. tube of a solution of an active substance is connected with ϕ , the angle of minimum deviation in a 60° prism, by the relation $\alpha = A\phi + B$. A and B are constants varying with the solvent, but A/B is nearly the same for different substances dissolved in the same solvent. He considers that A/B is closely related to the chemical nature of the solvent, and may be used as an aid in determining its constitution; his data, however, are in some cases not very satisfactory.

Perkin (135) has confirmed his previous conclusion that the magnetic rotation of hydrogen chloride in dilute aqueous solution is almost twice as great as when it is dissolved in

isoamyl oxide. At Jahn's suggestion Schonrock made experiments which seemed to show that this result was due to chemical action between the gas and the isoamyl oxide. Perkin finds, however, that there is no appreciable action even after three days, and he also finds that the rotation in alcohol is almost the same as in isoamyl oxide. These results clearly illustrate the difference in the behaviour of water and indifferent solvents.

As regards the colour of solutions, Sabatier (136) has determined the absorption spectra of solutions of cupric bromide, and Ostwald (137) has interpreted his results in terms of the dissociation hypothesis. On the other hand, Kastle (138) concludes that no known theory can explain the colour phenomena of salt solutions, and he attributes them to chemical processes. Magnanini (139) also finds that the salts of violuric acid do not agree with the dissociation hypothesis. He gives evidence which shows that the ions of the acid are colourless, whereas solutions of its alkaline salts are not colourless, but red. Again, on adding nitre to the solutions, the colour is not affected, although nitre should diminish the dissociation, and thus the colour of the solutions.

Buckingham (140) has tried to show that the fluorescence of salts may be correlated with their ionisation, and Bandrowski (141) considers that the light which is sometimes emitted during crystallisation is an electrical phenomenon associated with the ions, but in neither case is the evidence convincing.

Density and other properties.—The effect of temperature and pressure on the density of a solution, according to several papers (142) by Tamman, can be expressed by saying that the thermodynamic surface of a solution approximately coincides with that of the solvent if the zero of pressure in the case of the solution be taken to be not one atmosphere, as in the case of the solvent, but one atmosphere plus a definite pressure.

Kohlrausch and Hallwachs (143) have described an accurate method for determining the density of very dilute solutions, and obtained a series of values for saline solutions.

The densities of solutions of potash and soda have been determined by Pickering (144). In the case of soda the curves representing at constant temperature the variation of the density with the concentration show eight "breaks" at points corresponding with the composition of definite hydrates, six of which are known in the free state. The other two "breaks" correspond with those of the freezing-point curve. In the case of potash there are four "breaks," one of which occurs at a concentration corresponding with the composition of a known hydrate.

The volume change attendant upon neutralisation was found by Ruppin (145) to be additive in all the cases he studied, if allowance were made for the dissociation of the substances.

Solubility.—Of the numerous investigations on solubility, many of which refer to indifferent solvents, the most important is probably that of Etard (146), whose observations extend to temperatures as high as 700°. The concentration of a solution he takes as the weight of salt in one hundred parts by weight of solution, consequently his experimental curves represent the freezing-points of mixtures of substance and solvent, and the ends of the curves correspond with the melting-points of the pure substance and the pure solvent. In general, each curve both for water and other solvents consists of several straight lines. The observations refer to salts in water, mercuric chloride in thirteen organic solvents and cupric chloride in nine organic solvents. In the two latter cases evidence was obtained of combination between substance and solvent. Determinations were also made on sulphur in several organic solvents at temperatures up to its melting-point.

Lieben finds that the solubility of calcium, barium, and strontium salts of the normal fatty acids varies regularly with the replacement of H by Me. If the acids are not normal the variation is complex. Winkler's work on the relation between the solubility of a gas and the viscosity of its solvent has been examined by Thorpe and Rodger (148). They find that in the case of hydrogen, oxygen, and nitrogen, the diminution in solubility produced by rise in temperature

is proportional to the corresponding diminution in viscosity, and that the factor of proportionality is greater the greater the molecular weight of the gas.

According to Le Chatelier (149) the general law of the solubility of a normal substance should be independent of the nature of the solvent and should be given by

$$0.002 \log s - L/T + L/t = 0.$$

Here s is the number of molecules of substance in $s-1$ molecules of solvent, L and T the heat of fusion and melting-point of the substance, and t the freezing-point of the solution.

Küster (150) has attempted to find a convenient means of applying Nernst's method of determining molecular weights from diminution of the solubility. He uses as solvents phenol and a saturated solution of common salt, and finds how the solubility of the phenol is altered when different substances are dissolved in it, the amount of phenol dissolved by the salt solution being determined by titration. The results are fairly satisfactory, but have no pretensions to a high degree of accuracy.

From observations on the partition coefficient, Küster infers that iodide of starch is not a compound (151), and that when ether is absorbed by caoutchouc it exists partly as double molecules, which become fewer the more dilute the solid solution (152). By similar observations Schmidt (153) concludes that dyeing is not a case of solid solution, but is akin to absorption, and Jakovkin (154) studies the dissociation of potassium tri-iodide in aqueous solution.

In connection with colloidal solutions, Ramsden (155) finds that if a solution of albumen be shaken it coagulates and is only slowly soluble in water or salt solutions, and differs from albumen coagulated by heat. The change is not due to the chemical action of air.

CHEMICAL MECHANICS AND AFFINITY.

A detailed study of the mechanics of the reversible gaseous reaction involving the formation and decomposition of hydrogen iodide has been made by Bodenstein (156). At atmospheric pressure the fraction of the total hydrogen

iodide, which was decomposed when equilibrium was attained, varied with the temperature. At 290° it was 0.1637; at 518° , 0.2363; at 320° , however, it was only 0.1601, and a minimum occurred at this temperature. This remarkable fact points to the conclusion that at 320° the heat of formation is nil. Such a result is in harmony with thermochemical considerations, for at ordinary temperatures the heat of formation of hydrogen iodide is negative, while at high temperatures, since the amount of decomposition increases with the temperature, the heat of formation must be positive, and hence at some intermediate temperature it must be nil. Bodenstein also finds that pressure modifies the condition of equilibrium by increasing the decomposition. According to the law of mass action, pressure should produce no effect. Hence there is probably some secondary reaction involved whereby the volume of the system is diminished, and does not remain constant, as in the case of the normal reaction. The effect of pressure and temperature on the velocity of decomposition was also obtained; the velocity constant is almost proportional to the pressure.

Carrara (157) has studied the velocity of formation of Me_2EtSI . At 0° , if it be produced from Me_2S and EtI , the velocity constant is 0.00027, whereas if MeEtS and MeI be used the constant is 0.01223, or almost fifty times greater. Again if MeEt_2SI be formed from Et_2S and MeI , the constant is almost fifty times greater than it is when MeEtS and EtI are used.

The velocity of hydrolysis of ethers is definitely connected with their chemical nature; indeed, De Hemptinne (158) finds that if the constants for one series, and also that of a single member of another series, be known, the constants of all the members of the second series may be calculated. Certain reactions are of course only possible in certain solvents; an interesting study of the effect of the solvent has been made by Otto (159).

From observations of its influence on the saponification of methyl acetate, Walker concludes that in aqueous solution Na_2S exists as NaHS and NaHO (160). Using the rate

of inversion of sugar, Noyes and Clements (161) infer in a similar way that hydrogen potassium tartrate when dissolved yields a certain amount of free acid. The interaction of stannous chloride and ferric chloride has been shown by Kahlenberg to follow the law of mass action (162).

A reaction in a heterogeneous system has been studied by Carrara and Zoppellari. They find that on stirring water and sulphuryl dichloride by blowing air through the mixture, the reaction is of the first order, and the law of mass action is obeyed just as in a homogeneous system. The velocity is the same if decinormal potash solution be used, hence it is concluded that the water and not the potash effects the decomposition.

The affinity coefficients of a large number of bases have been obtained by Bredig (164) from observations on conductivity. The results show that of organic bases the quaternary are the strongest, and the ternary the weakest. The bases of P, As, Sb, S and Te are very strong, those of Sn and Hg are very weak. In the case of metameric diamines the base is the stronger the further the amido-groups are apart in the molecule.

A curious method of determining the affinity of feeble acids is due to Wood (165). It depends upon the inhibitory action which they exert on the velocity of hydrolysis of starch by diastase. Ostwald thinks the method may be useful in the case of feeble bases.

Linebarger (166) has described a method for measuring small dissociation-pressures like those of hydrated salts. The salt is brought into contact with ether and the amount of water given up to the ether determined by the rise in its boiling-point. The concentration of the water in the ether is thus obtained, and the dissociation-pressure of the salt is equal to the partial pressure of water in the vapour of a solution of this concentration. References to several new methods of determining transition temperatures are given on p. 319.

Continuing his previous experiments, Lea (167) found that on subjecting several easily reducible salts of metals,

such as silver, mercury, platinum, etc., to the prolonged action of high pressure amounting at most to 1,000,000 lbs. per square inch, a certain small amount of decomposition occurred, which was indicated by a darkening in the colour of the substances. The reactions involved are endothermic and the author concludes that the application of mechanical force can bring about such reactions. The results have given rise to a controversy (168) with Spring, in which both he and Lea claim to have been the first to show that mechanical energy can be continuously transformed into chemical energy.

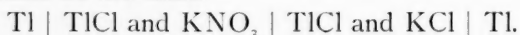
CHEMICAL ENERGY.

Thermochemistry.—Most of the work in thermochemistry has been concerned with the determination of thermal constants and does not admit of general treatment. An extensive investigation has been carried out by Stohmann and his pupils (169), who redetermine the heats of combustion of the fatty acids. Formic acid gives an exceptionally large value, and thus exhibits the behaviour which in general characterises the initial members of homologous series. Amongst the general conclusions they obtain, the most noteworthy are that on replacing H on a hydrocarbon by COOH the thermal change is variable, and that acetic acid has almost the same heat of combustion as malonic acid, and the same is true for corresponding homologues of the two series.

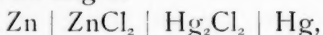
Berthelot (170) finds, as might have been anticipated, that the heat of reaction of bromine and propylene differs from that of bromine and trimethylene; the latter is considerably the larger. In another paper Berthelot has tried to reconcile his principle of maximum work with modern views of chemical energetics (171).

In a suggestive paper, Nernst (172) shows that, in general, on mixing two concentrated solutions which differ only as regards concentration the change in the free energy is equal to the change in the total energy of the system. From considerations of the vapour pressure and heat of dilution this is shown to be the case for solutions of sulphuric acid.

Electrochemistry.—The most important researches in electrochemistry have been concerned with the development of Nernst's theory, which is one of the most important advances of the new theory of solutions, an advance which enables the electromotive force of a cell to be correlated with the concentration of electrolytic solutions. The basis of the theory is the assumption that when a metal is immersed in a solution it exerts a definite solution pressure P , whereby ions tend to pass into the solution. This passage is opposed by the electrostatic attraction which it sets up, and also by the osmotic pressure p of ions of the same kind present in the solution. The larger P , other things being the same, the more strongly will the solution be positively charged and the electrode negatively charged. The potential difference between an electrode and a solution is held, therefore, to depend upon two constants, one of which, P , is due to the metal, and the other, p , to the cation concentration of the solution. If a cell be formed in which the electrodes are the same, P may be eliminated from the equations, and on neglecting the potential differences between the solutions, the E.M.F. may be expressed in terms of the osmotic pressures or the concentrations of the solutions around the electrodes. Goodwin (173) has made experiments on the chain—



Here as in the simple case the cation of the salt is the same as that of the electrode. He also makes observations on two chains consisting of



in which the concentrations vary, and which are opposed to one another. Here the solution around the electrode contains a sparingly soluble salt of the electrode in presence of another salt with the same anion. In both cases theory and practice agree, and a number of alterations in the solutions, such as the substitution of salts of other metals for those of potassium in case 1, or of bromides for chlorides in case 2, are found in accordance with theory to have no effect on the E.M.F.

The E.M.F., or the conductivity, is a convenient mode

of finding the solubility of difficultly soluble substances like silver iodide. Goodwin concludes that for solubilities less than 0.1×10^{-5} the E.M.F. gives better results than the conductivity. Smale (174) has made experiments to show that Nernst's theory applies as Ostwald has suggested to gas batteries. The electrodes were partly immersed in the gas and partly in the electrolyte, and the E.M.F. was found to be independent of the size of the electrodes and of the nature and concentration of solution, unless in the case of the halogen acids, where secondary reactions are supposed to occur. If hydrogen be put over two solutions of different concentration, the electrode in the stronger solution is positive. In the case of gas chains the E.M.F. and the solution pressure are inversely proportional to the absolute temperature.

Neumann has determined the potential difference between several metals, including hydrogen, and solutions of their salts. For equal concentrations of the metallic ion the nature of the negative ion had no influence on the E.M.F. On arranging the metals in the order of the potential differences obtained, it was found, as anticipated, that those metals coming after hydrogen, namely, Sb, As, Cu, Hg, Ag, Pb, Pt and Au, were all precipitated by hydrogen from their solutions. The potential differences between platinum and various oxidising and reducing solutions were also obtained, and out of forty cases only four gave positive differences. These were stannous chloride, sodium sulphide, hydroxylamine, and chromous acetate.

The potential differences between various metals and electrolytes have been measured by Rothmund, who uses a new method (176), and finds that the E.M.F. of a galvanic cell is the sum of the above potential differences, and that those between the two metals or the two electrolytes have an inappreciable effect on the E.M.F.

Streintz (177) has verified Nernst's conclusion that the E.M.F. of a Daniell's cell depends only on the ratio of the concentrations of the solutions of the two sulphates.

The potential difference between an aqueous solution

and another of the same salt in methyl alcohol, ethyl alcohol, or acetone, has been determined by H. C. Jones (178). The aqueous solution was always positive. The results indicate that the solution pressure of a metal varies with the solvent.

A paper by Nourisson, in which the E.M.F. was calculated from thermal data, has given rise to a discussion (179) involving a question of priority between Berthelot and Le Blanc. The main point to notice is that both Berthelot and Nourisson employ the old idea that the E.M.F. of a cell can be calculated from Thomson's rule on the supposition of the perfect transformation of chemical into electrical energy. Le Blanc points out that this view is now untenable.

In an extremely suggestive paper (180), entitled the "Chemometer," Ostwald deals with the question of chemical intensity. A thermometer measures the intensity of heat energy, an electrometer measures the intensity of electrical energy; a similar instrument in the case of chemical energy would be a chemometer. Ostwald points out that if we perform a chemical process in a voltaic cell, there is attendant upon it a movement of electricity, and work derived from the chemical process may be manifested as electrical energy. Now the electrical energy is equivalent to the chemical energy, and since the capacity factor of the electrical energy, that is, the quantity of electricity, is according to Faraday's law proportional to the capacity factor of the chemical energy, that is, the quantity of matter decomposed, it follows that the intensity factors must be proportional, and hence the electromotive force is proportional to the chemical intensity. In this way is the problem of the chemometer solved in the case of electrolytes. How it is to be done in the case of non-electrolytes, or by means of the other forms of energy into which chemical energy can be transformed, has yet to be seen.

Drude and Nernst (181) draw attention to a consequence of the electrostatic charges of the ions. If the dielectric constant of a medium increases on compression it will contract in an electrostatic field, consequently if free

ions exist in solutions of electrolytes the solvent will be compressed in the field produced by the ionic charges. The authors develop the theory of the subject, and recall the fact that as dilution proceeds the calculated molecular volume of a salt becomes less and less, and exhibits apparently the increased contraction of the solvent due to the increased ionisation. Several cases are quoted to show that the electrostriction thus produced by the dissociation of one gram-molecule of salt into two monovalent ions is almost the same, and varies between 8 and 11 c.c.

Photochemistry.—Rolloff (182) has studied the effect of light on the interaction of mercuric chloride and ammonium oxalate. Substances which increase the dissociation increase the amount of mercurous chloride produced. He concludes that only dissociated molecules take part in the reaction which is carried on by Hg and C_2O_4 ions. In the case of the interaction of bromine and oxalic acid in the light and in the dark he finds that the ratio of the velocities increases rapidly with the time, and on the addition of potassium bromide. In the potassium bromide solution KBr_3 is supposed to exist, and the action of light is held to increase the activity of the ions and the Br_3 group.

An attempt to explain the development of the silver bromide gelatine image of a photographic plate in terms of the intensity of reducing agents as found by observations on E.M.F., and by the application of the law of mass action, has been made by Bredig (183). Dewar (184) finds that at the boiling-point of liquid air photographic action is reduced by 80 per cent.

Lemoine considers that of the total light only $1/10,000$ th is used in chemical work in the reaction between ferric chloride and water (185).

An electrode consisting of a silver plate coated with silver bromide, which is sensitive to light, and which might probably serve therefore as an actinometer, has been described by Luggin (186). When paired with a silver plate in a solution of potassium bromide the results are, however, not very constant.

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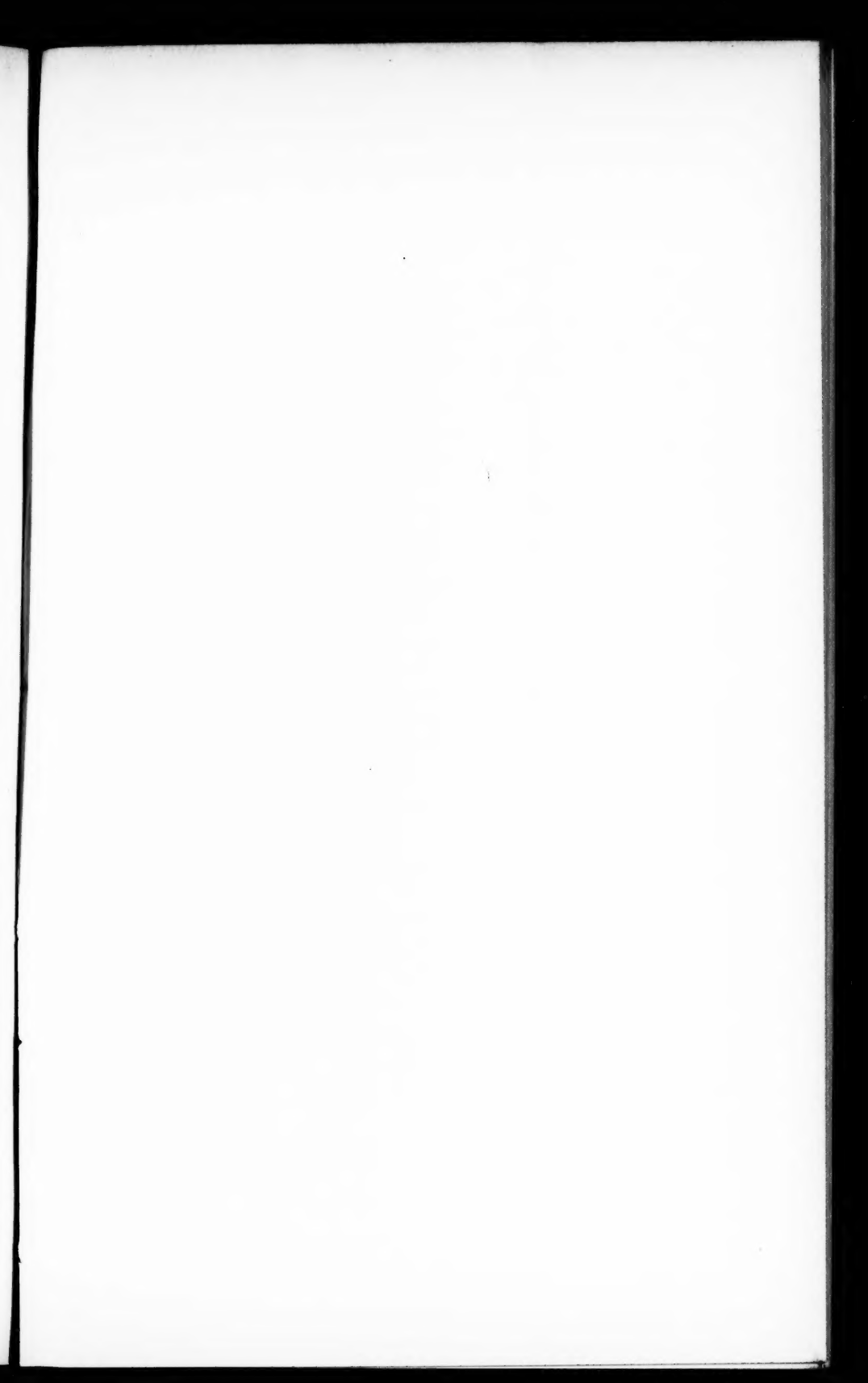
Electrochemistry:—

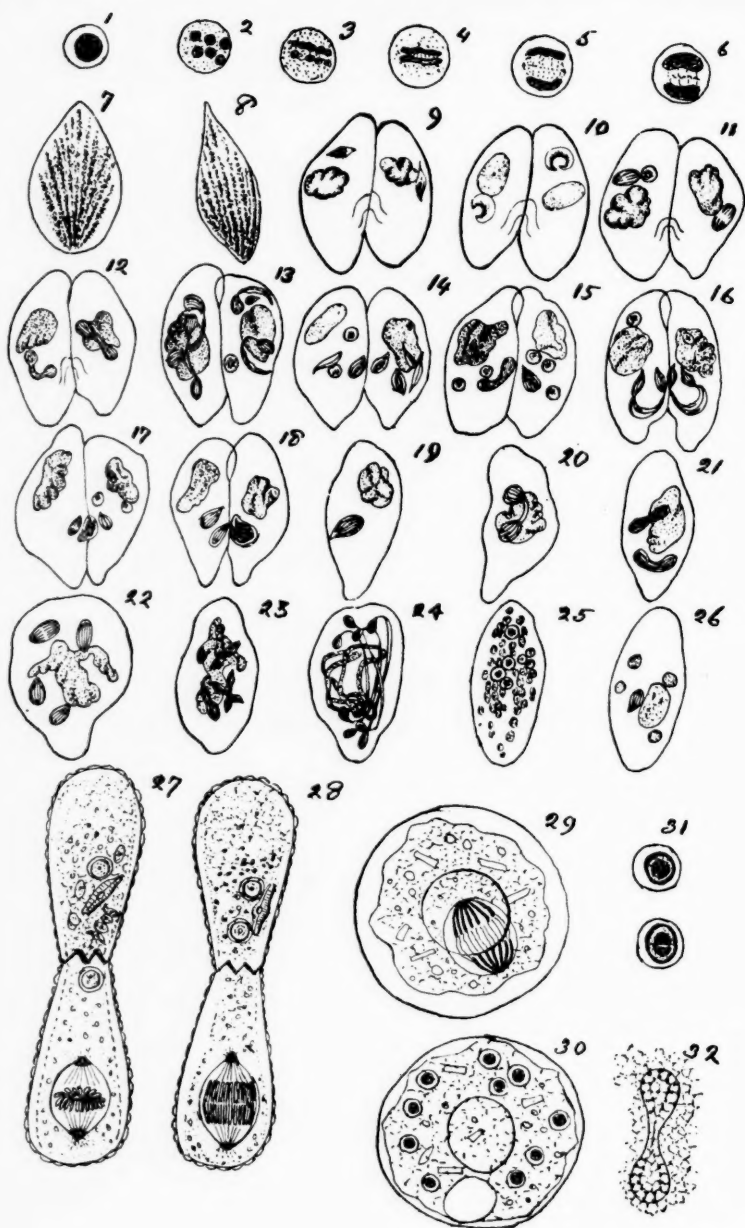
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ON THE PROTOPLASTID BODY AND THE METAPLASTID CELL.

IN the title which I had originally framed for the contents of this paper, the words proto- and meta-zoa stood in place of those employed, and I have made the change in terminology out of deference to certain criticisms which have reached me, concerning the impropriety of an indifferent use of the terms proto- and meta-zoa when speaking of both animals and plants.

The word "plast" has great advantages; without an affix it does not bind one to any numerical statement, and it is sufficiently vague to cover most anomalies that are likely to occur. Whatever it ought to mean, the really important matter of what it has come to mean may be gathered from the frequent use of the terms Mono- and Poly-plastid, to distinguish between two well-marked types of living forms. Of the first of these an *amœba* forms a typical example, and as the same structural elements which compose this organism apparently constitute the individual cells of the higher polyplastid forms, the constituents of the monoplastid body appear to be equivalent to those of the polyplastid cell. Plast becomes synonymous with cell, and the difference between mono- and poly-plastid organisms appears to be that the former are composed of one, and the latter of many cellular elements. Now, although the appreciation of this fact is exactly expressed by the current terms of multi- and uni-cellular organisms, I have not adopted these, because there are many monoplastid forms with affinities among the polyplastids, which, through such a definition, would be sharply excluded from them, and the inverse conclusion equally applies. Therefore I have simply retained the old affixes of proto and meta to designate the two great categories into which the various kinds of plastids appear to fall.

The term proto implies that the protoplasts preceded the metaplastids in point of time, and no objection is likely to be made to it on that account, although I doubt if the

assumed archaic character of the former rests on any surer basis than our inherent tendency to attempt to derive the complex from the simpler forms of life.

The outward semblance of the protoplastid body to the metaplastid cell is the somewhat insecure footing on which the cell theory set out to work its way into the complete ascendancy it enjoys to-day, and unless some of our most fundamental conceptions of the relationships between living forms are a delusion and a snare, there must exist somewhere beneath this outward semblance, a real community of structure which it is not unreasonable to expect that our enormously improved methods of investigation will suffice to show. In reality so much that is entirely new and strange has been lately added to our knowledge of the structure and life history of the protoplastids, and to the nature of the cyclical evolutions among the metaplastid cells, that it is by no means easy to say off-hand whether the cell theory has been weakened or supported by it all. The value of recent work in this direction may be perhaps best tested by the solutions it can be made to offer of the two great problems which have hitherto confronted the inquirers into the relation of the protoplastid body to the metaplastid cell, and these problems may be stated thus:—

1. There are forms of protoplastid which correspond in gross to the components of a metaplastid cell. Is the nuclear element in the former equivalent to the nuclear element in the latter?

2. The conjugating Infusoria, during their multiplication, go through a cyclical metamorphosis, and return at length to forms similar to those from which they started. Is there any evolution comparable to this in the successive development of metaplastid cells?

I shall discuss the bearing of recent work on these two questions in succession. As is well known, the nuclear element in many Rhizopods is a large round body, having about the same dimensions, relatively to the whole animal, that the nucleus of a metaplastid bears to the cell in which it is contained. According to the work of Gruber (1) and others, the nucleus in *Amœba* may become divided up into

a great number of daughter nuclei, the exact fate of which has not been ascertained; but the process of the successive multiplication of these nuclei appears to be carried on in a similar manner to the normal karyokinetic division of the nuclei in metaplastid cells (fig. 31). In *Actinospherium Eichhornii* the vesiculate resting nuclei (fig. 1) develop chromosomes or separate chromatic elements, and then go through the regular course of karyokinesis represented in figs. 2-6.

In the Rhizopod *Arcella* Gruber (2) represents the great nucleus dividing up in a typically mitotic fashion (figs. 29, 30), and during the fissiparous bipartition of *Euglypha alveolata*, Schewiakoff (3) has shown that karyokinesis, with its complement of chromosomes, spindle, and even centrosomes, is carried out in full (figs. 27-28).

Last, but not least, it is known that the great nucleus of many Rhizopods may increase by akinesis in the strictest sense of the term; and the nucleus of the Rhizopods (fig. 32) appears thus, even in the metamorphoses which it may undergo, to be strictly comparable to that of the metaplastid cells.

In the great majority of Infusoria, both ciliate and flagellate, the nuclear structures appear at first sight to be radically unlike those obtaining among metaplastid cells, because in these forms of protoplastids there are two kinds of nuclei, which, when they are fully formed, differ entirely from each other. The Macro—or larger of these two kinds of nuclei, multiply by a process practically equivalent to akinesis; while the Micro—Micro-nuclei pass through all the normal karyokinetic phases. It has been shown, however, by Maupas (4), R. Hertwig (5) and others, that the macro-nuclei of the Ciliate Infusoria arise periodically from more or fewer of the nuclei produced by karyokinetic division from the micro-nucleus; the elements which form the macro-nuclei being indistinguishable from those which persist as micro-nuclei when they are freshly formed. It consequently follows that the Ciliated Infusoria are to be regarded as multi-nucleate protoplastids, in which some of the nuclear elements have become structurally

changed. Thus the nuclear elements among the protoplastids multiply generally by karyokinesis, like the nuclear elements in metaplastid cells, and when this process is departed from, it varies in both proto- and meta-plastids towards akinesis in a similar way.

Now, when we consider the great complexity of the karyokinetic process, the long succession of complex structural changes by which it is brought about, and find that the same set of changes are gone through in the same order, during the division of nuclear elements as widely separated in the organic series as that of a *Euglypha*, and of the somatic cell of a Mammal, we are forced to the conclusion that the two series of phenomena have originated in common. It is inconceivable that two such long structural metamorphoses, corresponding throughout their whole cycle, should have been evolved independently at different times, and I see no escape from the conclusion that both the proto- and the metaplastid nuclei are structures which have had a common ancestry in the past. Further, as the relation of the nucleus to the cytoplasm of a *Euglypha*, or other protoplastid, differs in no way from that of the nucleus to the cytoplasm in a metaplastid cell, I accept, because I see no means of controverting it, the proposition that a protoplastid body is the morphological equivalent of a metaplastid cell.

With respect to the second problem, concerning the relation of the life cycle of the protoplastid to metaplastid development, the ascertained existence of conjugation among both ciliate and flagellate Infusoria is a factor of supreme importance, because it affords a common starting point, from which to compare the life cycle of the one and the individual development of the other. But before it is possible to regard the act of fertilisation in the proto- and meta-plastid in this light, it is necessary to be quite sure that the conjugation in the protoplastid is really a similar process to that occurring between the reproductive cells of higher forms.

It is well known that conjugation or fertilisation among the higher animals consists not so much in the fusion of two cells as in the fusion of certain cellular constituents, the

chief among which appear to be the nuclei. Now, in the Ciliate Infusoria it has been shown by the elaborate investigations of Maupas, and by the less complete, but in the main confirmatory work of R. Hertwig, that the primary object effected during conjugation of two individual ciliates, is the transference of nuclear elements from cell to cell, the process being accomplished in the following way.

Previous to conjugation, the body of a *Paramæcium* contains, as I have said, two kinds of nuclear elements—one large and more or less irregular, the other more rounded and definite in form. The larger, or macro-nucleus, remains unchanged, and takes no part in the ensuing transference, but the smaller, or micro-nucleus, goes through some extraordinary evolutions before the conjugative act begins. After the animals become applied together the micro-nuclei enlarge, and then elongate, the chromatic substance streaming to the broader end (fig. 7-8). Eventually both ends of the micro-nucleus become pointed, and the micro-nucleus, now enormously elongated, bends round upon itself in the manner represented in fig. 10, the chromatic substance being massed along the concave side. After a time, however, it again becomes rounded, the chromatin becoming aggregated into an equatorial plate of slender chromosomes, and the usual karyokinetic phases are gone through in succession. This division of the micro-nucleus is followed by another, so that there are eventually four daughter micro-nuclei in each conjugate, as the applied animals are called (figs. 11-14). Three out of these four daughter nuclei degenerate and disappear, and the one which remains in each is that which happens to be nearest to the oral aperture. These two remaining nuclei now divide again, and the resulting nuclei remain connected with one another with long filamentous strands (fig. 16), strangely similar to the connecting spindle filament I have elsewhere described in the divisions of sperm-mother cells of the Cartilaginous Fishes. In each conjugate one of the daughter nuclei remains nearer the oral aperture than the other (fig. 16), and these two nearer ones approximate more closely, and come eventually to lie together

in an intervening space (fig. 17). At the same time the filaments connecting the daughter nuclei of each animal disappear, and each of the two approximated nuclei passes from its parental animal into the other conjugate. In this way there are still two micro-nuclei in each conjugate, but one of them is indigenous to the animal in which it lies, while the other is derived from the opposite conjugating individual. The two micro-nuclei in either animal at first lie closely side by side (fig. 18), but eventually their investing membranes coalesce, and they fuse gradually together (figs. 18, 19). The process of conjugation is now complete, and there is one micro-nucleus in each conjugate, as represented in fig. 19.

Thus the essential process in the long metamorphosis is a transference of one micro-nucleus from each individual to the other, and the fusion of each of these transferred corpuscles with that which remains in its parental cell. The compound micro-nuclei thus produced are obviously similar to the nuclei of the fertilised ova in the higher animals and plants, and it is evident that the fertilisation process of the ciliates is in all respects identical with that obtaining among metaplastid cells. Thus it follows that the conjugation period among the Infusoria *can* be used as a point for comparison between the life cycle of these animals and the development of metaplastid cells; and it is possible further to compare the succeeding events in the Infusoria with the early developmental phenomena of the higher forms.

After the separation of the conjugates, the fertilised micro-nuclei in each *Paramacium* divide rapidly three times (figs. 20, 21, 22, 23), in such a way that of the eight residual nuclei four lie at one end of the animal and four at the other; and these nuclei, remaining some time connected with one another in pairs, give to the body of the animal the very curious appearance represented in fig. 24.

After a time the connections between these two groups disappear, and their respective characters—if not from the first inherently different—become subsequently changed. Those at one end grow large and macro-nuclear, while the

others remain micro-nuclear in character (fig. 25). Further, three out of each of the two groups of four nuclei eventually degenerate and disappear; and consequently the two remaining nuclei have the character of a micro- and a macro-nucleus respectively. Concomitantly with the above changes the old macro-nucleus has by this time almost entirely degenerated, and consequently the whole nuclear apparatus has returned again into the condition in which we found it, and the animal is ready to fissiparously bipartate once more.

It is by the rapid multiplication of individuals produced as described above that the familiar and intensely active communities of paramecia arise, and although they may be supplied with endless food and multiply amazingly for a time, it appears, according to Maupas, that their fissiparous multiplication has its limit. After this has been passed the communities diminish in activity, and the individuals composing them dwindle down in size, and I see no objection to the adoption of Maupas' view that such a community as a whole is undergoing senile degeneration, and that unless some new factor is introduced into the life cycle, it runs the risk of becoming eventually "*sans* everything". This factor consists in the periodic occurrence of conjugation in the manner I have just described: and it may take place either among individuals of the same, or, still better, between those of more or less remote communities, resulting in the rejuvenescence of the individuals which undergo it, and the completion of the infusorian life cycle.

Now in answer to the final question as to the relation between the cyclical evolutions of the protoplastids, and the successional formation of new cells in the development of metaplastid forms, it is well known that development in the latter proceeds, in the majority of cases, from a single fertilised ovum (which, as we have seen, is structurally identical with the body of a ciliate or other protoplastid, after conjugation has occurred), and it is carried on by the successive development and arrangement of cells which are also equivalent to the multitude of organisms produced by the successive bipartitions of a protoplastid form. Lastly, both

the fissiparous bipartitions of the protoplastids, and the successive cellular divisions in the developing metaplastid embryo, are brought about by complex nuclear metamorphoses in a similar way. Roughly speaking, therefore, and with certain reservations, of which I shall speak immediately, there appears to be an essential similarity between the process of cellular multiplication, by which the single complex individuality of a metaplastid is built up, and the fissiparous multiplication of independent protoplastid organisms. In the little green plant *Pandorina*, the fertilised ovum gives rise, by division, to three or four separate cells or protoplastid individuals, which, in turn, produce each sixteen daughter elements, and these do not separate from one another, but remain compounded into distinct metaplastid individuals with sixteen cells. After further multiplication of the cells of each of these individuals, the whole of the histological elements produced, separate from one another, and assume once more the form of true flagellate protoplastids, among which conjugation may occur, and the whole process is repeated.

Thus the development of a form like *Pandorina* is a process similar in its fundamental features to the life cycle of the protoplastid forms, and although, during the evolution, certain new characters are added to the fundamental and similar groundwork, by the formation of three or four metaplastid individuals, these apparently new characters may in reality be nothing more than a modification of the correlation existing among the individuals of a colony of protoplasts. Further, in a case like *Pandorina*, every cell of which the metaplastid is composed can, and usually does, give rise to more or fewer flagellate individuals, which after conjugation repeat the life cycle over again; but in many of the higher plants, and in all the metozoa, this capacity of every histological element to reproduce the parent species has been lost, and in most cases the faculty or power of the vast majority of the cells composing a metaplastid body, to return even to a flagellate or protoplastid form like the conjugating gametes of algæ has vanished also. The relegation of this power to certain tracts or repro-

ductive centres, may be viewed either as the cause or the consequence of the production of a highly specialised soma, somewhere along the life cycle, a soma which can be cast off and perish, so long as the original cyclical character of the metamorphoses in some elements of the organism is retained. It is shown, however, from the study of plants, that the development of the soma which constitutes their metaplastid individuality, may occur at different points anywhere along the course of the original life cycle; thus the soma which constitutes the ordinary fern plant is serially homologous with the plant or individual of a lily, but in the life cycle of a lily, after the formation of the sexual cells there is a limited developmental period, the elements produced in which correspond to those which build up the soma or plant of a fern prothallium and *vice versâ*. Moreover, in some cases, as in the ferns, more than one portion of the life cycle can be developed into a metaplastid plant, and the individuals thus arising may be told off to perform different functions in the economy of the whole cycle, and by their successional development, constitute the alternation of sexual and asexual generations. At the same time, as Huxley (6) pointed out years ago, when treating of the analogous phenomena presented by the various forms of Salps, "It cannot be too carefully borne in mind that zoological individuality is very different from metaphysical individuality, and that the whole question of the propriety of the 'Alternation theory,' as a means of colligating the facts (for at best it can be nothing more), turns upon the nature and amount of this difference".

"If the true definition of the zoological individual be (as the writer believes it to be) the sum of the phenomena successively manifested by, and proceeding from, a single ovum, whether these phenomena be invariably collected in one point of space or distributed over many, then there is no essential difference between the reproductive process in the higher and lower animals, and the alternation theory becomes unnecessary."

From all this, it would appear then, that the formation

of the protoplastid colonies, and the development of metaplastid individuals, are in their gross analysis, homologous processes; but when we try to push the comparison between them farther, when we try to ascertain which part of the protoplastid life cycle corresponds to any particular sexual or asexual generation in a metaplastid, it is obvious that without more data to go upon the attempt must fail, because between the acts of conjugation in both cases we have no fixed points from which to reckon. It is, for example, apparently impossible to say at present whether, at some point in the life cycle of a colony of *Paramœcia*, changes corresponding to the alternation of sexual and asexual generations of the metaplastids pass over all the members of the colony or not.

For some time, however, it has been known that among the higher plants the change from the sexual to the asexual generation is accompanied by profound changes in the characters of the cells composing them. Indeed, some such state of things might have been anticipated, from the fact that the number of the chromosomes in the nuclei of the cells of any particular species is definite and fixed. And since the act of conjugation consists in the fusion of two nuclei, it follows that this fixed specific number of the chromosomes must be doubled every time that conjugation occurs, or else the number of the chromosomes characteristic of the species must be periodically halved.

The latter of these two processes has been found to actually occur, but the manner of its occurrence has been, and still is, matter for the most profound dissent among zoologists and botanists alike. Botanical observers are, however, practically agreed to-day that, in spite of the repeated assertions of Weismann and his pupils to the contrary, the halving of the number of the chromosomes is not brought about by the extrusion of any nuclear elements at all, but occurs during the resting condition of the nuclei, the reduced number of the chromosomes simply appearing in the initial phases of the next division. In unison with this, Boveri found that in certain ovogeneses the number of the chromosomes was neither reduced in the divisions

which led up to the formation of the ovocytes, nor among those by which the polar bodies were extruded from these ovocytes, but that there were only half as many chromosomes present in these last divisions of the ovocytes as in the divisions before the first ovocyte was formed. Therefore the reduction must have taken place as in plants, during the rest following the division by which the first ovocyte was formed. Brauer (7) came to similar conclusions, both with respect to the ovogenesis of *Branchipus*, and the spermatogenesis of *Ascaris*, and I have myself shown in a variety of Mammals and Elasmobranchs, that the reduction of the number of the chromosomes takes place in resting cells, one or two generations before the formation of the spermatozoa, as the case may be. Moreover, the long series of structural changes in the resting nuclei, which lead up to the formation of the reduced number of chromosomes, and which I have termed collectively the *synapsis*, as well as the character of the chromosomes themselves, are so complex and peculiar as to leave no doubt that the halving of the number of the chromosomes, or synapsis, among all those animals which possess it, must have had a common origin in the past. Further, it has been shown by Farmer (7) that the structural details accompanying the synapsis among lilies, and more especially those of the chromosomes in the division immediately succeeding it, are extraordinarily similar to those existing at a corresponding period in the evolution of the reproductive cells of animal forms. These similarities constitute a fair basis for the assumption that the process may have been inaugurated before the animal and vegetable ancestry went apart, and has existed ever since.

We have then something actually before us which, in favouring the assumption of a common origin of the sexuality in animals and plants, actually invades the territory of the protoplastids themselves, because there are among these simple organisms forms which are as truly vegetable in their affinities, as there are others which are animal in theirs; and the synapsis, which appears to be common to both animals and plants, must have originated somewhere far back in the protoplastid ancestry.

It follows thus, that if the inferences I have drawn from these indisputable facts of histology are correct, that the synopsis should, and probably will, be found somewhere in the infusorial life cycle of to-day. Unfortunately the character of the nuclei of the Infusoria, the lack of the appreciation of the importance of such phenomena as I have just described, and more than anything, the Weismannistic conception of animal reduction, based as it is on O. Hertwig's erroneous observations, have hitherto left us in the dark concerning the existence or the non-existence of a synopsis in these forms. I have no doubt that with the modern methods of observation, we shall be able some day to pronounce definitely on the matter, and the knowledge, when it does come, will throw a most important light on future biological research.

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